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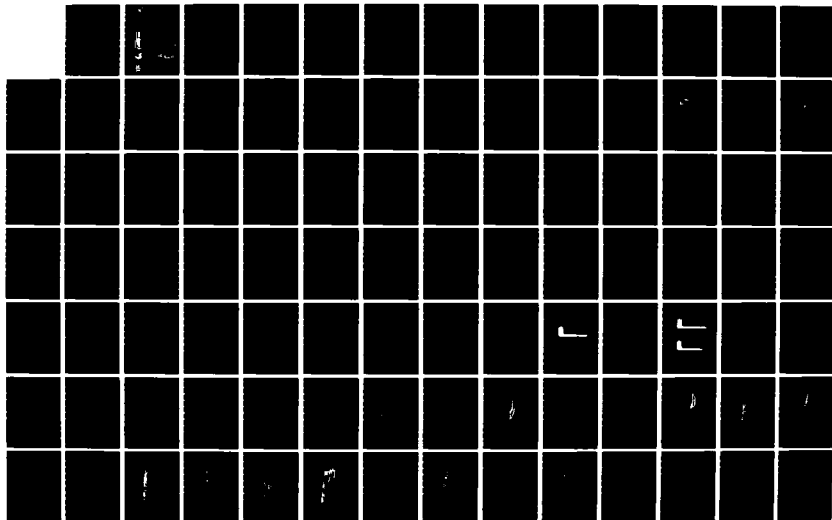
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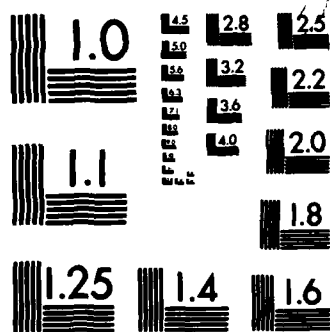
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GROUNDWATER CONTAMINATION RESPONSE GUIDE

Volume II: Desk Reference

J.H. GUSWA
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ACORN PARK
CAMBRIDGE, MASSACHUSETTS 02140

JUNE 1983

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known or suspected instances of contaminated groundwater, is described. The methodology provides a starting point from which information gathering and data collection actions can be initiated. While response actions remain site dependent, a general and logical approach to field activities is presented. An introductory summary of field investigative methods and analytical techniques, with data integration steps, appraises installation engineers of the complexities of field programs. Volume II: Desk Reference. A comprehensive survey of technical works resulted in this compilation of groundwater fundamentals and field investigation activities. Topical coverage ranges from hydrology basics to state-of-the-art equipment and field methods. Sufficient material is presented to acquaint the reader with basic concepts and fundamentals of groundwater and water quality issues. Numerous illustrations highlight these items. An applications-oriented review of field methods identifies equipment types and limitations. The essentials of geophysics, drilling methods, well construction, and sampling are addressed, with emphasis on integrating information in an iterative process to devise a cost-effective program. A review of contaminant transport in groundwater identifies significant parameters and physical systems of concern. Finally, a summary of groundwater treatment methods provides an options list for potential use. The report concludes with an agency address directory for water quality information and some representative cost schedules for field activities.

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PREFACE

This report was prepared by Arthur D. Little, Inc., Acorn Park, Cambridge, Massachusetts, under contract F33615-80-D-4002 for the Engineering and Services Laboratory, Air Force Engineering and Services Center (AFESC), Tyndall Air Force Base, Florida.

This report documents work performed between June and September 1982. The AFESC/RDVS project officer was Captain Glenn E. Tapio.

Several volumes of technical material were critically reviewed and compiled during preparation of this report. Expert summaries were provided by the following individuals:

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This report provides a review of equipment, methods, and technologies used in groundwater quality investigations. While serving as a current technology reference, the information will also provide input to developmental efforts leading to more efficient, durable, and cost-effective monitoring and remedial action technologies.

This report is not to be used for promotional or advertising purposes. Citation of trade names does not constitute an official endorsement or approval for use of such commercial products. The views expressed herein are those of the authors and do not necessarily reflect the official view of the publishing agency, the United States Air Force or the Department of Defense.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.


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SECTION I

INTRODUCTION

Since the mid-seventies, the emphasis on understanding the causes and effects of groundwater contamination by organic chemicals has increased because a few Air Force facilities have encountered significant problems with the presence of organic contaminants under their property. During investigation and cleanup of these known incidents, it became obvious that there was no organized procedure to guide Air Force personnel in determining the location, extent, and level of groundwater contamination, or to select the most appropriate containment or treatment technology. Because Federal legislation related to contamination of groundwater resources affects the Air Force, a methodology to assess and control groundwater pollution by organic chemicals became expedient.

The general problem with protection of groundwater resources is to identify the areas and mechanisms by which contaminants enter the groundwater system, to develop reliable methods for predicting contaminant transport, to select an appropriate contaminant/treatment technology, and to ensure compliance with federal and state legislation.

For Air Force personnel, this requires:

- identification and analysis of available information to estimate the extent, nature, direction, and rate of movement of the contaminated zone;
- development of a field investigation program to quantify the extent of contamination;
- selection of method(s) for containing the spread of contaminants or treating contaminated groundwater; and
- response to the appropriate federal and state agencies.

To effectively respond to groundwater contamination incidents, the Air Force is developing the capability to rapidly identify organic contaminants in groundwater, to determine pollutant pathways, and to determine the fate of organic constituents in groundwater. The results of this effort will [probably] be included in the Spill Prevention and Response Plan for each Air Force installation.

Until the Spill Prevention and Response Plan can be updated, an interim solution is needed. A user-oriented field manual, based on a literature review and describing the current best practicable

methodology for Air Force field personnel to respond to incidents of groundwater contamination by organic chemicals, is proposed.

This volume is designed to help base-level engineering personnel to address groundwater pollution problems in a logical manner. In particular, it addresses such issues as:

- the initial response to identified pollution incidents;
- developing a strategy for determining the origin of organic pollutants;
- determining the rate and direction of movement of the pollutants; and
- identifying possible strategies for control, containment, and cleanup of groundwater pollution.

This volume is not meant to provide specific solutions for groundwater contamination problems. The data necessary to design the response for a particular contamination incident must be developed from site-specific soil and groundwater investigations. It does, however, describe an overall approach which can be followed to ensure a logical, scientifically based response to a groundwater pollution incident.

The following sections provide the technical base for field response development and preparation. This volume is based on a thorough review of the scientific and technical literature related to groundwater contamination and summarizes the state of the art of the various techniques used to identify, quantify, and respond to groundwater pollution incidents.

SECTION II

GENERAL DESCRIPTION OF GROUNDWATER CONTAMINATION

1. OVERVIEW OF GROUNDWATER HYDROLOGY AND CONTAMINATION

a. Groundwater Hydrology

Groundwater is the name given to water moving through the land-based portion of the hydrologic cycle (Figure 1). Water in the ground fills pores in sediment or cracks in rocks and usually moves slowly along indirect paths around each particle. About 4 percent of the total world volume of water is groundwater; however, groundwater constitutes between 68 percent and 99 percent (depending on the sources) of all useable fresh water (Table 1). At present, the United States is using 25-percent groundwater (water recovered from permeable aquifers) and 75-percent surface water for its water supply (Figure 2). The Western United States constitutes the bulk of groundwater use with 45-percent groundwater and 55-percent surface water (Freeze and Cherry, 1979). The increasing need for clean sources of fresh water and the long return period for replenishment or cleaning of groundwater explain the recent emphasis on protecting the purity of groundwater.

In the subsurface all gradations exist between freely flowing water and water firmly fixed in the crystal structure of minerals. Figure 3 is a schematic of these gradations; however, there are no sharp boundaries between the various water types. Soil water, readily evaporated on a hot day, grades into intermediate vadose or suspended water. Intermediate vadose water, in turn, grades slowly to capillary water in silts and clays although there is a distinct boundary between these water types in coarser grained sediments. The boundary between vadose water and groundwater is known as the water table. Davis and DeWiest (1966) define the water table as follows:

"The most common definitions of the water table state that it is the surface separating the capillary fringe from the 'zone of saturation,' or that it is the surface defined by the water levels in wells which tap an unconfined saturated material. A more exact definition states that the water table is the surface in unconfined material along which the hydrostatic pressure is equal to the atmospheric pressure."

The water below the water table is known as groundwater, the saturated zone or phreatic water. Because the lower portions of the vadose zone may be saturated with capillary water, phreatic water is the better synonym for groundwater (Figure 3). Figure 4 shows the major water zones superimposed on a topographic profile (Bear, 1979).

TABLE 1. ESTIMATE OF THE WATER BALANCE OF THE WORLD

Parameter	Surface area (km ²) × 10 ⁶	Volume (km ³) × 10 ⁶	Volume (%)	Equivalent depth (m)*	Residence time
Oceans and seas	361	1370	94	2500	~ 4000 years
Lakes and reservoirs	1.55	0.13	<0.01	0.25	~ 10 years
Swamps	<0.1	<0.01	<0.01	0.007	1-10 years
River channels	<0.1	<0.01	<0.01	0.003	~ 2 weeks
Soil moisture	130	0.07	<0.01	0.13	2 weeks-1 year
Groundwater	130	60	4	120	2 weeks-10,000 years
Icecaps and glaciers	17.8	30	2	60	10-1000 years
Atmospheric water	504	0.01	<0.01	0.025	~ 10 days
Biospheric water	<0.1	<0.01	<0.01	0.001	~ 1 week

*Computed as though storage were uniformly distributed over the entire surface of the earth.

Source: Freeze, R.A. and J. A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

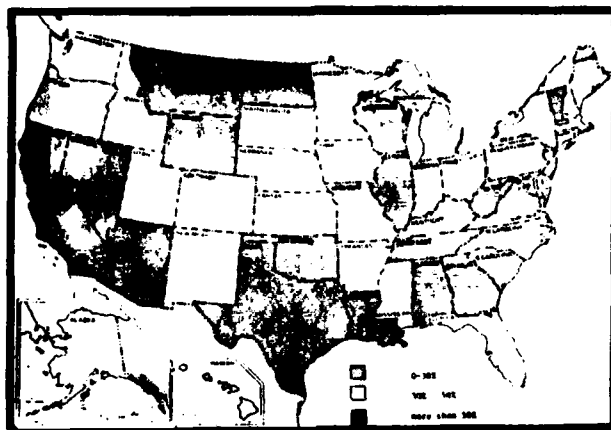


Figure 2. Percent of Population Served by Groundwater

Source: Bartlet, R.E., "State Groundwater Protection Programs -- A National Summary," Ground Water, Volume 17, Number 1, pp. 89-93, © 1979.

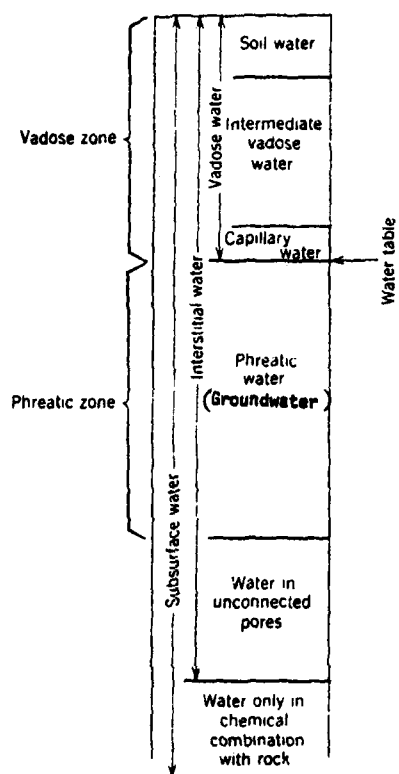


Figure 3. Classification of Subsurface Water

Source: Davis, S.M., and R.J.M. DeWiest, Hydrogeology, John Wiley and Sons, Inc., © 1966.

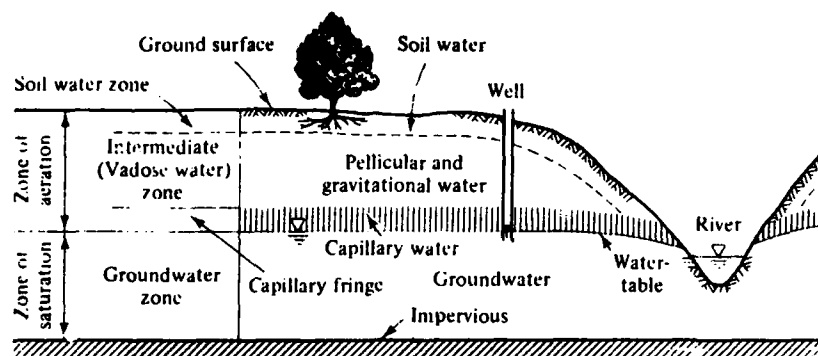


Figure 4. The Distribution of Subsurface Water

Source: Bear, J., Hydraulics of Groundwater, McGraw-Hill Book Company, New York, © 1979.

Within the groundwater system, water occurs and moves through the void spaces of the geologic materials. These void spaces may be the intergranular porosity of unconsolidated materials or the fractures and solution cavities commonly found in consolidated material. The volume of water contained within any particular geologic unit and the ease with which it moves through that unit depends upon the frequency, size, and degree of interconnection between the void spaces. The term aquifer is applied to the geologic units through which water generally moves easily, and the term confining bed is applied to those units through which water movement is generally restricted. The term "leakage" is commonly used to describe the exchange of water between aquifers and confining beds.

Aquifers are subdivided into two general categories: confined or unconfined. Confined aquifers are commonly referred to as artesian aquifers and unconfined aquifers are commonly referred to as water table aquifers. The classification of confined or unconfined aquifers is based on the absence or presence of a water table or free water surface. An unconfined aquifer is one in which the water table acts as the upper surface of the zone of saturation. Confined aquifers are under pressure greater than atmospheric and bounded above and below by confining beds. The water level of a well which penetrates a confined aquifer will rise above the base of the overlying confining bed. The water level in the well is referred to as the piezometric or potentiometric level and corresponds to the hydrostatic pressure level of water in the aquifer. If the piezometric level is above ground level, a flowing well results.

Water moves through the ground from areas of recharge to areas of discharge. For unconfined aquifers, the source of water recharge that infiltrates the unsaturated zone is a portion of the precipitation that falls on land surface. For a confined aquifer, the source of water is commonly leakage through an overlying or underlying confining bed and from surface infiltration where the confined aquifer is exposed at land surface. Groundwater discharge areas are commonly surface water bodies, such as streams, marshes, and oceans.

As water moves downward through the unsaturated zone, it may encounter zones where its rate of downward movement is slowed. This can result in localized zones where all the void spaces are saturated with water. Such a condition is referred to as a perched water table condition. Figure 5 illustrates the types of aquifers and the relationship between aquifer and confining beds and recharge and discharge areas.

Aquifers are characterized by their ability to conduct water under a hydraulic gradient and by their ability to store water. Hydraulic conductivity (K) is a measure of the aquifer's ability to conduct water under a hydraulic gradient. It is a property of the geologic medium and the fluid flowing through it. Aquifer transmissivity (T) is a measure of the ability of an aquifer to transmit water through its entire thickness and is equal to the product of the conductivity and aquifer thickness ($T=Kb$). The storage coefficient (S) is a measure of the

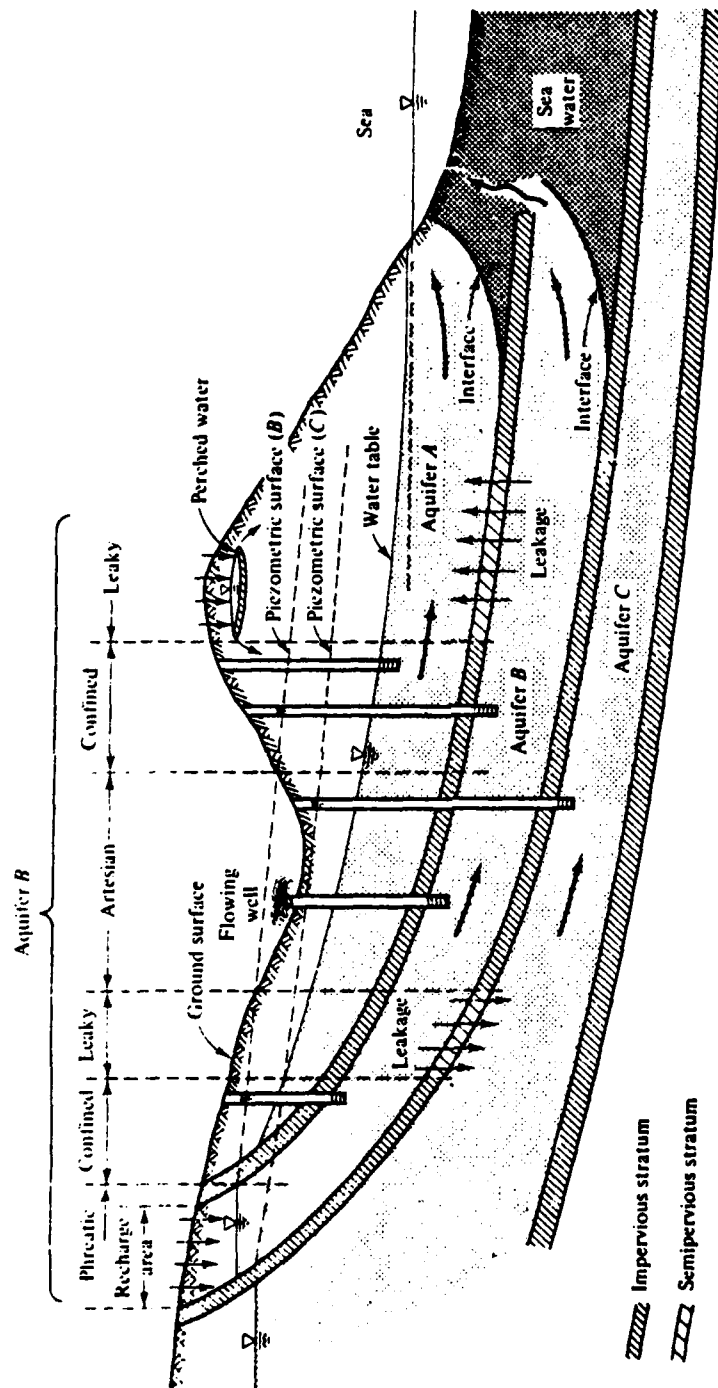


Figure 5. Schematic Hydrologic Section Showing Aquifers, Confining Beds, Recharge and Discharge Areas, and Perched Water Table Conditions.

Source: Bear, J., Hydraulics of Groundwater, McGraw-Hill Book Company, New York, © 1979

volume of water than an aquifer releases from or takes into storage in response to a change in piezometric head. For confined aquifers, the storage coefficient ranges from 5×10^{-3} to 5×10^{-5} and is a measure of the fluid and rock compressibility. For unconfined aquifers, the storage coefficient ranges from 0.1 to 0.3 and is an indicator of the aquifer pore space volume.

Groundwater movement can be predicted using Darcy's Law, which can be expressed in the following way:

$$q = \frac{Q}{A} = -K \frac{\Delta h}{\Delta X} \quad (1)$$

where

- q is the Darcy velocity (L/T)
- Q is the flow rate (L³/T)
- A is the cross sectional area perpendicular to the flow direction (L²)
- K is the hydraulic conductivity (L/T)
- Δh is the total potential head change (L)
- ΔX is the distance across which the head change occurs (L)

The Darcy velocity, q, is essentially unidirectional, is based on the total cross-sectional area, and does not represent the true velocity of the individual water particles that follow irregular paths around individual grains (Figure 6). The true velocity or seepage velocity is determined by dividing the Darcy velocity by the effective porosity of the geologic medium. If, for example, the effective porosity were 0.20, then the seepage velocity would be five times faster than the Darcy velocity. This is not the true velocity of every water particle because it does not consider the flow path followed but it is a good estimate of the average velocity.

Prediction of the rate and direction of movement of contaminants in groundwater, begins with evaluation of the simple flow system, specifically, the variables in Equation 1. The next step is to analyze the effect that the local geology has on the flow system. The CEQ (1981) states that:

"The degree of threat to groundwater [becoming contaminated] depends on the material underlying the surface site and the particular geologic and hydrologic conditions. For example, a dump sited on top of a thick layer of impermeable clay poses little threat to an aquifer beneath it, but a landfill on permeable material is a serious threat."

As the critical variables are defined at a particular site, the simple flow law (Darcy's law) is expanded upon to better model the given

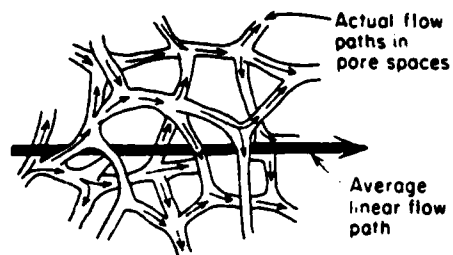


Figure 6. Average Linear Velocity Compared With Actual Flow Paths of Groundwater Around Grains

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

situation. With every increase in required input data, more extensive field methods must also be used to fully evaluate the site.

The subsequent sections of this report are designed to show how each of the preceding variables as well as variations in properties of the contaminants themselves can affect the overall transport of contaminants in a groundwater system. Defining and evaluating the most critical variables at a given site are the most important steps in defining the extent of contamination and predicting future movement of contaminants.

b. Groundwater Contamination

Because groundwater is becoming so widely used for drinking water, preventing and detecting its contamination has become increasingly important. Although filtration and chemical reactions between contaminants and sediment or rock cleanse many potential pollutants from percolating groundwater, larger concentrations and more inert chemicals often preclude this self-cleansing mechanism (CEQ, 1981). Soluble contaminants may move more quickly in groundwater than the average water flow thus causing a large volume of groundwater to be polluted. Insoluble or immiscible fluids often do not move as rapidly as the average water flow, and may, therefore, persist as in contaminants in an area for a long time.

The normal components of clean groundwater may include any of the long list of possible inorganic ions listed in Table 2. The levels of any specific chemicals considered objectionable depend on the use of the water. Tables 3 and 4 list concentration limits for various inorganic and organic water constituents. The list for drinking water standards (Table 3) is longer and has smaller recommended concentrations than Table 4, the standard for agricultural water. Water with concentrations exceeding these limits would be considered polluted for that use. The severity of the problem of groundwater pollution is highlighted by the rapid increase in development of manmade organic compounds to a total number now near 2 million (Freeze and Cherry, 1979).

Organic chemicals make their way to the land surface as potential groundwater contaminants as a result of the use of pesticides, the use of land for sewage disposal, the use of sanitary landfills or refuse dumps for disposal of organic compounds, burial of containers with organic compounds at special burial sites, leakage from liquid waste storage ponds, and accidental spills along highways, or storage and handling areas. Figure 7 shows the interactions between sources of organic chemicals and the hydrologic cycle.

TABLE 2. CLASSIFICATION OF DISSOLVED INORGANIC
CONSTITUENTS IN GROUNDWATER

Major constituents (greater than 5 mg/l)	
Bicarbonate	Silicon
Calcium	Sodium
Chloride	Sulfate
Magnesium	Carbonic acid
Minor constituents (0.01-10.0 mg/l)	
Boron	Nitrate
Carbonate	Potassium
Fluoride	Strontium
Iron	
Trace constituents (less than 0.1 mg/l)	
Aluminum	Molybdenum
Antimony	Nickel
Arsenic	Niobium
Barium	Phosphate
Beryllium	Platinum
Bismuth	Radium
Bromide	Rubidium
Cadmium	Ruthenium
Cerium	Scandium
Cesium	Selenium
Chromium	Silver
Cobalt	Thallium
Copper	Thorium
Gallium	Tin
Germanium	Titanium
Gold	Tungsten
Indium	Uranium
Iodide	Vanadium
Lanthanum	Ytterbium
Lead	Yttrium
Lithium	Zinc
Manganese	Zirconium

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

TABLE 3 STANDARDS FOR DRINKING WATER

Constituent	Recommended concentration limit* (mg/l)
Inorganic	
Total dissolved solids	500
Chloride (Cl)	250
Sulfate (SO_4^{2-})	250
Nitrate (NO_3)	45†
Iron (Fe)	0.3
Manganese (Mn)	0.05
Copper (Cu)	1.0
Zinc (Zn)	5.0
Boron (B)	1.0
Hydrogen sulfide (H_2S)	0.05
Maximum permissible concentration‡	
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	0.01
Chromium (Cr^{VI})	0.05
Selenium	0.01
Antimony (Sb)	0.01
Lead (Pb)	0.05
Mercury (Hg)	0.002
Silver (Ag)	0.05
Fluoride (F)	1.4-2.4§
Organic	
Cyanide	0.05
Endrine	0.0002
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
2,4-D	0.1
2,4,5-TP silvex	0.01
Phenols	0.001
Carbon chloroform extract	0.2
Synthetic detergents	0.5
Radionuclides and radioactivity	
Maximum permissible activity (pCi/l)	
Radium 226	5
Strontium 90	10
Plutonium	50,000
Gross beta activity	30
Gross alpha activity	3
Bacteriological	
Total coliform bacteria	1 per 100 ml

SOURCES: U.S. Environmental Protection Agency, 1975 and World Health Organization, European Standards, 1970.

*Recommended concentration limits for these constituents are mainly to provide acceptable esthetic and taste characteristics.

†Limit for NO_3 expressed as N is 10 mg/l according to U.S. and Canadian standards; according to WHO European standards, it is 11.3 mg/l as N and 50 mg/l as NO_3 .

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

TABLE 4. RECOMMENDED CONCENTRATION LIMITS FOR WATER USED
FOR LIVESTOCK AND IRRIGATION CROP PRODUCTION

	Livestock: Recommended limits (mg/l)	Irrigation crops: Recommended limits (mg/l)
Total dissolved solids		
Small animals	3000	700
Poultry	5000	
Other animals	7000	
Nitrate	45	—
Arsenic	0.2	0.1
Boron	5	0.75
Cadmium	0.05	0.01
Chromium	1	0.1
Fluoride	2	1
Lead	0.1	5
Mercury	0.01	—
Selenium	0.05	0.02

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

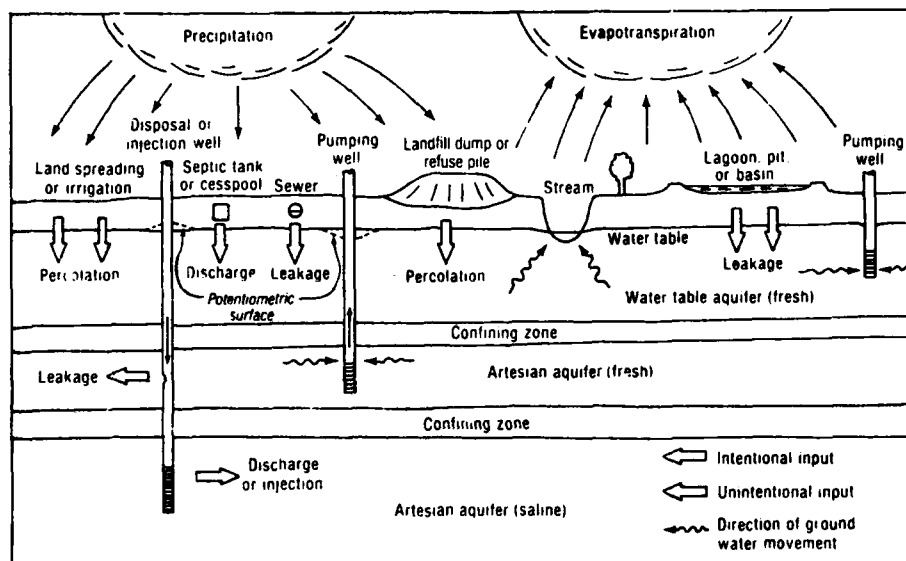


Figure 7. Sources of Groundwater Contamination

Source: CEQ, 1981.

2. CAUSES AND PREVENTION OF GROUNDWATER CONTAMINATION

a. Introduction

Groundwater is contaminated by the movement of pollutants through an aquifer recharge zone into the aquifer. Pollutants percolate through a recharge zone which usually includes a soil layer. The soil layer may partially cleanse percolating water of contaminants by biologic degradation, adsorption, and ion exchange processes. However, soils are not capable of removing many synthetic organic compounds such as chlorinated solvents. In fact, a study in New Jersey found that groundwater toxic organic contamination paralleled surface water toxic organic contamination (Page, 1981). Groundwater contamination can also be caused by the following: contact between contaminated surface waters and groundwater (i.e., wetlands); disposal of contaminants below the high groundwater table (i.e., deep-well disposal); and subsurface discharges from leaky pipes, storage tanks, etc. (Freeze and Cherry, 1979).

Contaminants in a groundwater system will slowly disperse in and move with the groundwater. Typically groundwater moves at a rate of 5 to 500 feet per year (Environmental Science and Technology, 1980). Groundwater can be pristine within a few hundred feet of contaminated water because the laminar flow characteristics of groundwater are not conducive to mixing and dilution of contaminants (CEQ, 1981). Although groundwater moves slowly, contaminants may travel long distances over long periods of time since little degradation or dilution takes place in the anaerobic groundwater environment.

Landfills and chemical dump sites have received the most attention as a sources of groundwater contaminants. The disposal of industrial wastes in impoundments and solid waste sites was identified in a 1977 EPA report as the major cause of groundwater contamination (U.S. EPA, 1977a). Other significant sources of contamination include:

- surface impoundments (e.g., wastewater lagoons);
- mines;
- septic systems;
- underground petroleum storage tanks;
- spills;
- the intentional application of pesticides; and
- runoff from paved areas and piles (e.g., coal, salt).

A number of these sources are depicted in Figure 7.

Prevention of groundwater contamination requires that contaminants not be allowed to travel through an aquifer recharge zone and that spread of contaminants be contained. Preventive measures include:

- removal of contaminants from the recharge zones;
- restriction or diversion of water movement with barriers to isolate the contaminants; and
- collection of the contaminated leachate.

In this section we describe, in general terms, the causes and prevention of groundwater contamination. Prevention of groundwater contamination due to past disposal practices is the focus rather than protection strategies at new disposal facilities. Examples are cited wherever possible.

An extensive bibliography of reports, manuals, and books on spill control and groundwater contamination prevention is included at the end of this report.

b. Sources

(1) Land Disposal

(a) Causes

Groundwater may be contaminated by migration of surface water associated with the land disposal site into the aquifer and/or percolation of liquid waste disposed at the site into the aquifer (Figure 7). An unlined land disposal facility situated over permeable geologic material in an aquifer recharge zone is likely to cause groundwater contamination. Many land disposal facilities sited prior to the Resource and Recovery Act (RCRA) may be in locations where the hydrogeologic environment is conducive to transport of contaminants to the groundwater. A study of 50 industrial disposal sites indicated that a large number of the approximately 50,650 active and inactive land disposal sites may be contaminating groundwater (CEQ, 1981). Groundwater at 40 of the 50 sites surveyed during the study contained organic solvents, benzene, and chlorinated phenols.

(b) Prevention

Containment of contaminants above the groundwater table or isolation of the contaminants from the groundwater flow are prevention methods. The location of the contaminants in relation to the groundwater table is an important containment consideration. If the contaminants are above the water table, the reduction of surface infiltration and/or collection of leachate and other percolating liquids can be used as prevention techniques. Available technologies to reduce surface infiltration include surface seals, surface water diversions and graded surfaces.

Lowering of the water table and groundwater diversion techniques can prevent contamination below the groundwater table. Groundwater may be adjusted to below the contamination level by either pumping or

subsurface drains. It is necessary to ensure contaminants do not percolate down to the lowered water table level. Diversion techniques include upgradient and downgradient diversions or barriers. Upgradient diversions or barriers prevent groundwater from contacting the contaminants while downgradient diversions contain groundwater which has contacted the contaminants. Available diversion and barrier technologies include slurry walls, grout curtains, and sheet pile barriers. Diversion techniques may also be applicable to contaminants located above the groundwater table.

(2) Surface Impoundments

(a) Causes

Leakage of contaminants through the bottom of surface impoundments is the principal cause of groundwater contamination associated with this source. An estimated 26,000 industrial surface impoundments are currently in operation (Wyss, 1980). A survey of over 8000 sites indicated that: 50 percent of the impoundments may contain hazardous contaminants; and 10 percent are unlined, overlie permeable material, and are within 1 mile of a water supply well (CEQ, 1981).

(b) Prevention

Lining surface impoundments to prevent leakage is a relatively recent engineering practice. Low permeability clays or synthetic materials are typically used for liners. If a liner begins leaking it may be possible to repair; however, liner repair feasibility has not yet been demonstrated. Therefore, lined surface impoundments which leak should be treated as unlined facilities in most cases.

The first step toward preventing a leaking surface impoundment from contaminating groundwater is generally to drain the impoundment. After dewatering, prevention of further groundwater contamination will require the same technologies as those cited in the land disposal section.

(3) Mines

(a) Causes

Mines have been used for the disposal of hazardous materials in the past. Groundwater flows to subsurface mine walls, through the mine caverns where it can entrain contaminants, and back to a surface or groundwater system.

(b) Prevention

Groundwater barriers may be an effective technique, but implementation would require an extensive hydrogeologic survey because of the complexity of water movement in mines. Lowering the water table adjustment may be a more cost-effective prevention alternative.

(4) Septic Systems

(a) Causes

Many homeowners clean septic systems with fluids which contain such chemicals as trichloroethylene (TCE), benzene, or methylene chloride. The fluids dissolve sludge in the septic system so it is transported through the soil absorption field. Both the dissolved sludge and the cleaning fluid can percolate down to the groundwater levels along with other mobile components of the leachate. Each homeowner may use less than a gallon per cleaning but the cumulative use by 19.5 million owners of onsite disposal systems (CEQ, 1980) can be significant. For example, the aggregate annual use of septic system cleaning fluids on Long Island, New York was on the order of 400,000 gallons (CEQ, 1980).

(b) Prevention

Septic system cleaning fluids pose a significant groundwater contamination prevention problem because of the great number of small sources which must be controlled. Eliminating the use of septic cleaners which contain potential groundwater contaminants is probably the most cost-effective prevention measure which can be taken. The State Legislation of New York has considered banning the use of septic cleaners which contain certain organic solvents (NYDEC, 1979).

(5) Underground Petroleum Tanks

(a) Causes

Leaking underground petroleum tanks pose a groundwater contamination threat. Gasoline contains aromatic hydrocarbons and lead which can be hazardous to humans if consumed. For example, in Nassau County, New York, 36 leaking gasoline storage tanks were identified in 1979 (NYDEC, 1979).

(b) Prevention

Groundwater pumping to collect and purify the groundwater near a leaky tank is the usual course of action (NYDEC, 1979). The tank itself may be excavated and repaired or replaced to prevent a chronic groundwater contamination.

(6) Spills

(a) Causes

Spills of toxic materials generally occur during transportation or storage of the materials. A spill in a hydrogeologic area favorable for quick migration to a groundwater system can pose a major problem.

(b) Prevention

When spills are reported promptly, many techniques exist to clean them up. Cleanup technologies include removal and in-situ treatment. The U.S. Environmental Protection Agency maintains a technical assistance team to respond to spill cleanup needs.

3. CASE HISTORIES

The following three case histories provide examples of how groundwater contamination incidents were identified, the problems assessed, and remedial actions proposed or undertaken at three Air Force Bases. They represent contamination by trichloroethylene (TCE), benzene, and petroleum, oil, lubricant (POL).

a. Case Study #1: TCE Contamination

(1) Background

Trichloroethylene (TCE) contamination of groundwater was discovered in 1977, at a midwestern Air Force base. The Base overlies a sand and gravel aquifer which overlies a thick clay layer at an average depth of 65 feet. The water table ranges from 10 feet below the land surface at the western part of the base to 25 feet at the eastern part. The TCE contaminated groundwater flows northeast under the influence of the natural groundwater gradient and base water supply wells toward a nearby lake.

TCE is a degreasing solvent and is a suspected carcinogen. The U.S. Environmental Protection Agency (EPA) estimates that the incremental increase of cancer risk over an individual's lifetime is 10^{-6} when drinking water concentrations of TCE are 2.7 micrograms per liter (USEPA, 1980). According to information supplied by the Air Force, the EPA is currently considering a TCE drinking water standard of 4.5 micrograms per liter, and the National Academy of Science suggests a maximum concentration of 270 micrograms per liter in drinking water at USAF bases.

(2) Problem Identification

In October 1977, the Base Civil Engineering Squadron received complaints about the peculiar odor and taste of the drinking water at the base. Analysis of faucet water showed a TCE concentration of 1,100 micrograms per liter. In addition, analysis of water taken directly from a supply well in the eastern part of the base showed a TCE concentration of 6,700 micrograms per liter.

The suspected source of contamination was an underground 500-gallon tank used for temporary storage of waste TCE. Approximately 5,000

gallons of TCE had been added to the tank, and an unspecified amount had been pumped out of the tank since 1962. Upon discovery of contamination, the tank was excavated and a leak discovered where the filler pipe connected the tank. Further investigation of base water supply wells indicated TCE contamination at various locations throughout the base. Analyses of offbase water supplies showed no contamination except for one well located 1,000 feet east of the base. These analyses and the discovery of a leak in the TCE storage tank pointed to the tank as the major source of TCE contamination.

Following the discovery of TCE contamination, use of water supply wells in the eastern portion of the base was discontinued in favor of wells in the southern portion. In January 1978, two of these wells were again put into use when they were found to have only trace amounts of TCE contamination. Later in 1978, TCE was detected in the southern wells, and their use was also discontinued. Only one other water supply well was affected by TCE.

(3) Problem Assessment

Late in 1979, the U.S. Geological Survey (USGS) began collecting data with the installation of wells in areas of known contamination. Over the study period, the USGS installed 165 wells -- 116 four-inch diameter wells used for pumping tests, water level measurements, and collection of water samples for analysis; and 49 wells 1 1/4 inches in diameter, used only to measure water level. Information from the wells and other sources of data was used to:

- 1) determine the rate and direction of groundwater movement;
- 2) determine the horizontal and vertical extent of TCE contamination;
- 3) investigate all suspected sources of TCE, past and present; and
- 4) develop and calibrate mathematical models to predict groundwater and TCE movement and provide information in deciding how to remove the contamination.

This allowed the USGS to develop an effective remedial program.

The Air Force and USGS investigations also revealed other contamination problems at the base which were unrelated to the TCE storage tank leak. These included TCE contamination from other sources, dichloroethylene contamination from an unknown source, and contamination of groundwater by a fuel substance. Although these problems were discovered in the course of the investigation, they will not be further discussed.

(4) Remedial Action

Initial efforts to control TCE contamination were made prior to the involvement of the USGS. In March 1978, two of the eastern water supply wells were pumped to remove (or purge) TCE-contaminated water. Purged water was treated in aeration reservoirs near the water supply treatment plant. In addition, three new purge wells were added in May 1978, and three more in August 1979. These wells had removed approximately 535 gallons of TCE by June 1980. Their effectiveness, however, had greatly decreased. While 215 gallons of TCE were purged from September 1978 to August 1979, only 75 gallons were purged between September 1979 and August 1980.

Based on USGS analyses, therefore, three new purge well sites were identified. Groundwater models were used to determine the optimal pumping rates for the purge well system and predict its effect on TCE contamination. The models indicated that the central part of the plume would be lowered 15 feet and that water north, east, and south of the most highly contaminated zone would be drawn into the wells. TCE, therefore, would not escape eastward toward the lake. The three new purge wells have recently been constructed and have been operating since May 1982. No information on their effectiveness is yet available.

b. Case Study #2: Benzene Contamination

(1) Background

Benzene contamination of groundwater was discovered in the late 1970s at an Air Force base in the northern United States. Benzene is used in the synthesis of organic chemicals and as a solvent and degreasing agent. It is a component of aviation fuels, gasoline, lacquers, and paints. The EPA estimates that the incremental increase of cancer risk over an individual's lifetime is 10^{-6} when drinking water concentrations of benzene are .66 micrograms per liter (USEPA, 1980a). Benzene contamination is considered significant in this case because it is thought to indicate the presence of JP-4 fuel or gasoline in the groundwater.

(2) Problem Identification

Benzene concentrations exceeding 1000 micrograms per liter were discovered in a well during the investigation of another groundwater problem at the base. Water from an adjacent deeper well had benzene concentrations from 96 to 197 micrograms per liter. This indicated local contamination caused by surface storage. Laboratory analyses showed that the water not only contained benzene, but toluene and other unidentified organic compounds as well.

The suspected source of contamination was the base motor pool which has surface tanks for bulk storage of JP-4 fuel. Samples of JP-4 fuel

and gasoline from the motor pool were analyzed to try to verify the source of contamination. These results were inconclusive because of the decomposition of the organic compounds in the groundwater. Comparison of gas chromatograph spectra, however, suggested JP-4 fuel as the most likely contaminant.

(3) Problem Assessment

Current data available are insufficient to predict the distribution and movement of contaminated groundwater. Only the general direction of groundwater flow is known. Additional work is required to adequately assess the contamination problem at this site. This will include installing deep and shallow wells in the path of groundwater flow and developing a mathematical flow model. These will be used both to predict the distribution and movement of contaminated groundwater and to design and evaluate purge pumping schemes.

(4) Remedial Action

No remedial action activities have been carried out at the site to date. However, purge pumping wells may eventually be installed to remove the contaminated groundwater.

c. Case Study #3: POL Contamination

(1) Background

POL and other types of groundwater contamination were discovered at a number of sites at an Air Force base in an arid region. The Base is located over a major aquifer system which has complex hydrologic conditions, including fluctuating water levels and continually changing aquifer conditions. Extensive groundwater pumping in the region has a significant effect on the pattern of groundwater flow.

Three sites located at the Base are of particular interest. Site A is the location of an underground POL storage tank which leaked unspecified amounts of POL to groundwater. Site B is the location of a jet fuel pipeline break which occurred in the late 1960s. Approximately 250,000 gallons of jet fuel leaked to the ground surface. 100,000 gallons of this may have been recovered, leaving 150,000 gallons available for seepage to groundwater. There is, however, no permanent water table below the site. Site C is the location of a leaky hydrant at the end of a fuel line. An estimated 50,000 gallons of jet fuel leaked to the ground surface and possibly to groundwater in the mid-1970s. These sites represent the major sources of groundwater contamination at the base.

(2) Problem Identification

The Base is located in an area of significant groundwater resources. It was, therefore, important to identify potential sources of groundwater contamination due to spills (such as Sites B and C) and

disposal practices (Site A). These investigations were the result of Air Force concern about known sources of potential contamination of a sensitive groundwater area.

(3) Problem Assessment

The first stage of problem assessment was to identify potential contamination of groundwater and soil at these sites. This involved installing three monitoring wells at Sites A and C, and two soil borings at Site B downgradient of the sites. Drilling locations were based on local topography, geology, available well logs, and USGS water level data.

Based on the results of analyses of samples from wells and soil borings, additional wells or borings may be required before a remedial action decision can be made. For example, if wells at Site A indicate POL contamination, more wells will be required to delineate the areal extent of contamination. Additional soil borings would also be required at Site B to determine the extent of soil contamination.

(4) Remedial Action

Two basic options exist for remedial action at these sites. If the site is found to have POL or fuel floating on the groundwater surface, these materials could be removed by means of a double pumping system. One pump in the double pumping well lowers the water table around the well while the other, a skimming pump floating on the water surface, removes the floating contaminants.

On the other hand, if the site is contaminated with organic vapors, a "no action" plan may be used. Over time, natural diffusion processes should release these vapors to the atmosphere. The time involved, however, may be extensive, and the vapors may continue to represent a potential source of groundwater contamination. Although expensive, three-dimensional computer simulations of the diffusive processes, based on detailed geologic data, can be developed to estimate the amount of time required. The "no action" option could also be used if the contamination is immobile or if the potential for further contamination is not too severe. Periodic monitoring is required for this option. Specific remedial action options proposed for these three sites include:

(a) Site A

- seal abandoned wells which may cause contamination of deeper aquifers used for base water supply;
- empty the remaining underground storage tanks to avoid the potential of additional leakage;
- option of either removing the POL by a double pumping system or performing no remedial action with monitoring. Choice depends on the

characteristics of the contamination, as discussed above.

(b) Site B

- Alternative 1: If the fuel is confined by geologic conditions (a bedrock "knob") injection of water could cause the fuel to rise to the top of the water where it could be recovered by a double-pumping system.
- Alternative 2: Accelerate the vaporization of the fuel by moving air through the soil (air sweeping) and collecting the vapors by means of a vent system.
- Alternative 3: No remedial action with monitoring.

(c) Site C

Either remove the fuel by air surface of water bodies or moist soil, or in precipitation, acquire enough energy through solar radiation to escape the liquid phase and pass into the gaseous state. Sublimation differs from this only in that the water molecules are converted from the solid phase (snow or ice) directly to vapor, without passing through the liquid form. Transpiration is the process by which water absorbed by vegetation is evaporated into the atmosphere from plants' surfaces. When measuring the amounts of water being circulated into the atmosphere, it is usually very difficult to distinguish how much is contributed solely by evaporation and how much is contributed solely by transpiration. The two processes, therefore, are often considered together as evapotranspiration.

4. REGULATORY SUMMARY

a. Introduction

The guidelines for responding to groundwater pollution are based on the legislation which gives the federal government (primarily through the EPA) and the states authority and responsibility to control

groundwater pollution. The primary federal legislation which pertains to groundwater is summarized in Table 5 and described briefly below.*

b. Federal Statutes

(1) Resource Conservation and Recovery Act of 1976
(RCRA)

RCRA amends the 1965 Solid Waste Disposal Act and outlines the federal government's program to manage solid and hazardous wastes and establish standards for treatment, storage, and disposal of hazardous wastes. The Act's guidelines are directed toward the protection of water users rather than groundwater, but the federal government's role in controlling the sources of groundwater contamination (land disposal of municipal waste and all aspects of hazardous waste) was increased. RCRA provides for the permitting of disposal facilities and a "cradle to grave" manifest system for hazardous wastes.

In addition, the new regulations for land disposal facilities (40 CFR 264) set groundwater protection standards for new and existing facilities. This standard has four parts (Inside EPA, 1982):

- Hazardous chemicals are to be monitored and removed if necessary.
- Maximum concentration limits established in the Safe Drinking Water Act will be used as groundwater standards where possible. Otherwise, there is to be "no increase over background levels."
- Standards must be met at the edge of the waste management area (the compliance point).
- If standards are exceeded, a corrective action program must be submitted and implemented until the standard has not been exceeded for a period of 3 years (the compliance period).

(2) Comprehensive Emergency Response, Compensation and Liability Act of 1980 (CERCLA, or Superfund)

CERCLA authorizes federal and state governments to remove hazardous substances and wastes and perform remedial actions at sites that are a danger to public health and welfare or the environment. Section 101(3) defines the environment as including " . . . groundwater, drinking water

* These summaries are based primarily on "The Federal Response to Ground Water Protection" by Kevin McCray, Waterwell Journal, Volume 36, Number 6, pp. 42-3; and memoranda between the EPA Administrator and the Ground Water Policy Group, published in the Environmental Reporter, The Bureau of National Affairs, Inc., 6/25/82, pp. 292-3.

TABLE 5. SUMMARY OF FEDERAL LEGISLATION PERTAINING TO GROUNDWATER

<u>Act</u>	<u>Emphasis</u>	<u>Applicability to Groundwater Response</u>
RCRA	Sources of contamination	Monitoring and cleanup requirements at disposal facilities
	Controlled sites	Response to contamination at RCRA-permitted sites
CERCLA	Remedial Action	Response to contamination at sites not permitted under RCRA
	Uncontrolled sites	
Clean Water Act	Protection of surface waters	Notification requirements for spills, any discharge of hazardous wastes or waste constituents in reportable quantities
		Establishes reportable quantities for hazardous materials
Safe Drinking Water Act	Sets maximum concentration levels	Regulates use of injection wells
		Protection of sole-source aquifers
Surface Mining Control and Reclamation Act	Protection from adverse effects of mining operations	Hydrologic studies required
		Provides for alternate water supply when mining disrupts groundwater supply of an adjacent landowner

TABLE 5. (CONCLUDED)

<u>Act</u>	<u>Emphasis</u>	<u>Applicability to Groundwater Response</u>
TSCA	Manufacture, distribution and use of hazardous materials	Gives EPA regulatory authority over hazardous materials which may affect the environment
Uranium Mill Tailings Radiation Control Act	Active and inactive uranium mill tailings site	Establishes standards for all environmental media
FIFRA	Pesticide control	Gives EPA responsibility to control pesticides

supply, land surface or subsurface strata, or ambient air within the United States . . ."

(3) Safe Drinking Water Act of 1974

This Act authorizes EPA to set maximum contaminant levels and monitoring requirements for public water systems. It also regulates the uses of underground injection wells to protect drinking water aquifers and provides for the protection of sole-source aquifers. The EPA Administrator may designate an aquifer as the sole or principal drinking water source if contamination "would create a significant hazard to public health." According to the Act, no federally funded projects may be constructed which would lead to the contamination of a designated sole-source aquifer.

(4) Clean Water Act

This statute is actually a series of amendments made in 1972 and 1977 to the Federal Water Pollution Control Act of 1948. The stated purpose of the Act is to "restore and maintain the chemical, physical and biological integrity of the nation's waters." Its emphasis, however, is on surface ("navigable") waters. The Act seeks to eliminate the discharge of pollutants into navigable waters by 1983, and establish national policies to prohibit the discharge of toxic pollutants in toxic amounts and to develop area-wide waste treatment management planning. Discharge to groundwater must be considered in the Comprehensive Programs for Water Pollution Control (Section 102) and the Area-wide Waste Treatment Management Plans (Section 208). Section 402 establishes a requirement that the states control the discharge of pollutants into wells, and Section 303 requires the states to establish groundwater quality standards where it is shown that groundwater has a "clear hydrologic nexus" with surface water. The Act also establishes notification requirements for hazardous chemical spills.

(5) Surface Mining Control and Reclamation Act of 1977

This Act gives the Department of Interior authority to protect the public and the environment from the adverse effects potentially caused by surface and underground mining operations. Hydrogeologic studies are required prior to the covering or burial of hazardous materials as well as when mines are to be used for the disposal of any type of waste material. In addition, if mining activities seriously disrupt the groundwater or surface water supply of an adjacent landowner, an alternative water supply must be provided.

(6) Toxic Substances Control Act (TSCA)

This Act authorizes the EPA to restrict or prohibit the manufacture, distribution, and use of products which may adversely affect health and the environment. While groundwater is not

specifically mentioned, it is assumed that "the environment," which is defined in Section 6(e), includes groundwater.

(7) Uranium Mill Tailings Radiation Control Act

This Act establishes health and environmental standards for active and inactive uranium mill tailings sites. The standards protect "public health, safety and the environment" and apply to all media, both above and below ground, including groundwater.

(8) The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

This Act gives EPA responsibility for the control of pesticide use. Environmental impacts of pesticide use must be considered in the registration process, including effects on groundwater quality.

c. Notification Requirements

Response to groundwater pollution problems depends primarily on the types of facilities involved. Three possibilities are likely:

(1) Discovery of Groundwater Contamination While Monitoring an RCRA-Permitted Facility

This case falls under the RCRA regulations found in 40 CFR 265.93-4.

- If contamination is in wells upgradient of the site (i.e., background concentrations have changed) this should be reported in the annual report required under 40 CFR 265.75.
- If contamination is found and confirmed in downgradient wells, the EPA Regional Administrator must be given written notice, within 7 days of the confirmation, "that the facility may be affecting groundwater quality." In addition, within 15 days after the notification, a plan for a groundwater quality assessment program which has been certified by a qualified geologist or geotechnical engineer must be submitted to the Regional Administrator. The plan must specify:
 - the number, location, and depth of wells to be used;
 - sampling and analytical methods for those hazardous wastes or hazardous waste constituents in the facility;

- evaluation procedures, including use of previously gathered groundwater quality information; and
- a schedule of implementation.

The plan must then be implemented and used to determine:

- the rate and extent of migration of the waste or constituents in the groundwater; and
- the concentrations of waste or constituent in the groundwater.

Within 15 days after the determination is made, a written report must be submitted to the Regional Administrator containing an assessment of the groundwater quality. If no waste or constituents are determined to have entered the groundwater, this is indicated in the above report and the assessment program is discontinued. If wastes or constituents have entered the groundwater, then groundwater quality assessments and reports to the Regional Administrator must be continued on a quarterly basis until final closure of the facility.

(2) Discovery of Groundwater Contamination Related to a Facility not Permitted Under RCRA

This case falls under 103a of CERCLA. If one pound or more of hazardous waste or a reportable quantity of wastes specified under 40 CFR 117.3 is determined to have been released in a 24-hour period, the National Response Center should be notified "by means of rapid communication." If notification in this manner is impractical, alternate officials have been designated. Officials to notify, therefore, in order of priority are:

1. Duty Officer, National Response Center, U.S. Coast Guard, 400 7th Street, S.W., Washington, D.C. 20590. 800-424-8802.
2. The On-Scene Coordinator as specified in the Regional Contingency Plan for the geographic area in which the discharge occurs.
3. Commanding Officer Office-in-Charge of any Coast Guard unit in vicinity of the discharge.
4. Commander of the Coast Guard district in which the discharge occurs.

This notification is also appropriate for hazardous material spills or any reportable hazardous materials discharge.

(3) Discovery of Groundwater Contamination not Related
to Any Known Source

In this case, neither RCRA nor CERCLA directly apply. However, it is recommended that the procedure in Case 2 be followed so that the National Response Center can determine which government agencies to notify.

In addition to notification requirements under federal legislation, states may also have notification requirements. The state Board of Health or the Public Health Department should be contacted to find out the specific requirements of the state in which the facility is located.

d. Developing Issues

Two policies which are now being developed by the EPA may also affect the regulations of groundwater and the response to groundwater pollution. The first is the EPA's Ground Water Protection Policy, expected to be released by September 30, 1982. This policy is expected to emphasize that "states should have the lead role in groundwater protection." Each state will be asked to develop a groundwater protection strategy "commensurate with each state's own needs" by the end of FY 1984 (Environmental Reporter, 6/25/82, pp. 290-293). These strategies may make notification of groundwater pollution more specific and more stringent at the state level.

The second policy is being developed by the EPA in conjunction with the Department of Defense. The goal of the policy is to protect the environment while taking into account "the important national security ramifications" of environmental issues. This may make response requirements for defense facilities less stringent in certain circumstances than for other facilities. The EPA and key Congressional leaders, however, are opposed to exempting the Defense Department from complying with environmental laws. The Department of Defense currently has a special status regarding environmental response. It has primary authority for responding to releases of hazardous substances for its own facilities and cannot use Superfund monies for long term remedial action activities. It can, however, use Superfund for emergency response (Environmental Reporter, 5/28/82, p. 91). Response procedures to groundwater pollution could eventually be affected by this policy change.

5. CHARACTERIZATION OF POLLUTED GROUNDWATER

Following the identification of a groundwater contamination incident, characterization of the polluted groundwater is desired in one or more ways, including:

(1) Extent and degree of contamination (i.e., how much groundwater has been polluted and how badly);

(2) Altered potential for groundwater use (e.g., is groundwater fit for drinking, for irrigation, or for process water);

(3) Treatability (i.e., to what extent might the groundwater be treated by various methods).

In all cases, groundwater sampling and analysis will be required to assess the degree of contamination. However, characterization under Items (b) and (c) (following paragraphs) will require substantially more chemical-specific analyses than for Item (a).

a. Extent and Degree of Contamination

Samples collected from various locations (e.g., wells, springs), at various depths, and at various times can be used, in conjunction with relatively rapid and inexpensive tests, to generally assess the extent and degree of contamination.

Portable instrumentation, some with small probes that can be lowered into wells, is available to measure such parameters as pH, specific conductance, dissolved oxygen, total organic carbon, and individual anions (e.g., Cl^- , NO_3^- , SO_4^{2-}) or cations (Na^+ , K^+ , Ca^{++}) that may show altered or elevated concentrations due to contamination. Specific conductance is an especially good indicator for many (but not all) classes of soluble pollutants since it is rapid (small probes are available for in situ measurements) and will reflect the presence of inorganic ions and highly soluble organics which, because of their high mobility, will be at the forefront of the plume of contaminated groundwater.

Other simple indicators of groundwater contamination include: (1) color, odor, and taste; (2) organic vapor concentration, which can frequently be monitored with small, semiconductor-type probes; and (3) measurements of the amounts of (organic) material that can be extracted with such solvents as methylene chloride or chloroform.

In all cases, it is necessary to obtain data over a wide enough area around the site of suspected contamination to clearly establish background levels of the selected parameters. With a good data base, it will frequently be possible to establish not only the extent and degree of contamination, but the flow direction of the plume of contaminated groundwater.

b. Altered Potential for Groundwater Use

To assess to what degree a contaminated aquifer may still be useful, it will be necessary to obtain chemical-specific analyses of the water to be used. In general, although there are exceptions, the highest standards (and thus the lowest allowable concentrations or criteria) will apply to drinking water, with lower standards applying to

livestock water, irrigation water and (industrial) process water, in turn.

A characterization or classification with regard to the potential for use will seldom be a simple task since water quality criteria and standards have been set for only a limited number of chemicals, and the focus has been on the protection of drinking water and aquatic life; much less attention has been given to criteria and standards for irrigation, livestock, and process water.

Some of the documents which may be of help in a use-classification include the following:

- EPA's 1980 Water Quality Criteria Documents (USEPA, 1980a) which "contains recommended maximum permissible pollutant concentrations consistent with the protection of aquatic organisms, human health, and some recreational activities." The documents cover 64 of the 65 pollutants designated as toxic under Section 307(a)(1) of the Clean Water Act (i.e., the priority pollutants).
- EPA's Quality Criteria for Water (the "Red Book") (USEPA, 1976a). The Red Book provides recommended criteria levels focusing on the protection of aquatic life and domestic water supplies. In a few cases, separate criteria are listed for agricultural or industrial uses. The report focuses on inorganics (mostly metals) and pesticides. This book should be used only if the chemicals are not covered by the 1980 criteria (EPA, 1980).
- Water Quality Criteria, 1972 (the "Blue Book") (NAS, 1972). This major study by the National Academy of Sciences (NAS) for the EPA provides major sections on criteria for the protection of: (1) recreation and aesthetics; (2) public water supplies; (3) fresh water aquatic life and wildlife; (4) marine aquatic life and wildlife; (5) agricultural uses of water (livestock and irrigation); and (6) industrial water supplies. The coverage of organics, except for some pesticides, is small.
- Drinking Water and Health (NAS, 1977). This is an important review of the problems associated with chemicals in drinking water with important conclusions (similar to criteria) for many classes of pollutants. For organics, the report covers 74 nonpesticides (chosen from a listing of over 300 that have been found in drinking water) plus 55 pesticides.

- EPA's National Interim Primary Drinking Water Regulations (USEPA, 1976b). These primary standards cover only a few pesticides within the general class of organic compounds.
- EPA's National Secondary Drinking Water Regulations (USEPA, 1979a). These regulations cover properties or pollutants that may adversely affect the aesthetic quality of drinking water, such as taste, odor, color, and appearance. The proposed secondary levels represent federal goals, but are not federally enforceable.

It should be noted that the criteria published by the EPA are not legally enforceable standards. In general, only states can set water quality standards; however, they must be at least as stringent as the EPA criteria. The state should always be contacted for the latest standards applicable to the site of a groundwater contamination incident. In addition, both the EPA and the Food and Drug Administration have standards for (pesticide) residues in food which should be consulted if irrigation uses are contemplated.

The Clean Water Act requires the states to review and revise their water quality standards at least once every 3 years. While all states have a set of water quality standards, they are often highly variable in nature, and their coverage of toxic organics at present (except for some pesticides) is minimal.

In the absence of federal or state criteria and standards for specific chemicals, it may be necessary for special literature searches and/or laboratory tests to be conducted. If sufficient data exist, the calculation of a preliminary pollutant limit value (PPLV) may be carried out as described by Doore et al., 1980. The PPLV value is a temporary, nonregulatory value that is based on information available in the literature and which relates primarily to human health effects.

c. Treatability

Characterization of polluted groundwater with regard to treatability is discussed in Section VI ("Groundwater Treatment Methods").

SECTION III

FACTORS AFFECTING CONTAMINANT TRANSPORT

1. HYDROLOGIC CYCLE

Water is present on the earth in the oceans, in the atmosphere, on the surface, and in the ground. The complex system whereby water moves these environments is called the hydrologic cycle. A general understanding of all aspects of the hydrologic cycle is essential to understanding its subsurface.

The earth's hydrologic cycle is driven by the heat of the sun and the pull of gravity. For example, at the surface of the oceans, water is heated by the sun, vaporizes, and escapes to the atmosphere. Conversely, water vapor in the atmosphere can be cooled and condensed as water droplets, which fall to the earth's surface. Water's circulation system is a complex loop, with many interconnections. Figure 8 illustrates this system. The following is an overview of the various means of transfer of water through the hydrologic cycle.

Water is released to the atmosphere through the combined actions of evaporation, transpiration, and sublimation. These are three variations of the same process driven by heat energy from the sun. According to Davis and DeWiest (1966), evaporation, or vaporization, is "the process by which molecules of water at the surface of water bodies or moist soil, or in precipitation, acquire enough energy through solar radiation to escape the liquid phase and pass into the gaseous state. Sublimation differs from this only in that the water molecules are converted from the solid phase (snow or ice) directly to vapor, without passing through the liquid form." Transpiration is the process by which water absorbed by vegetation is evaporated into the atmosphere from plants surfaces. Commonly, when measuring the amounts of water being circulated into the atmosphere, it is very difficult to distinguish how much is contributed solely by evaporation and how much is contributed solely by transpiration. The two processes, therefore, are often considered together as evapotranspiration.

The amount of water vapor which the atmosphere is capable of holding at any given time is a function of air temperature. As air temperature increases, the atmosphere's vapor capacity increases. As air temperature decreases, however, the atmosphere's vapor capacity is lowered and the excess water vapor condenses on small particles of dust or of salt that are also in the atmosphere. The principal way of decreasing air temperature is to lift the air higher in the atmosphere, and there are a number of ways to accomplish this. For example, winds blowing clouds toward mountain ranges carry the clouds upward over the mountainous obstacle. Similarly, when a warm, light air mass meets a cooler, heavy air mass in the atmosphere, the lighter one must rise over the obstacle of the heavier one. Finally, the earth's radiational cooling heats the air near the surface of the earth, causing it to rise.

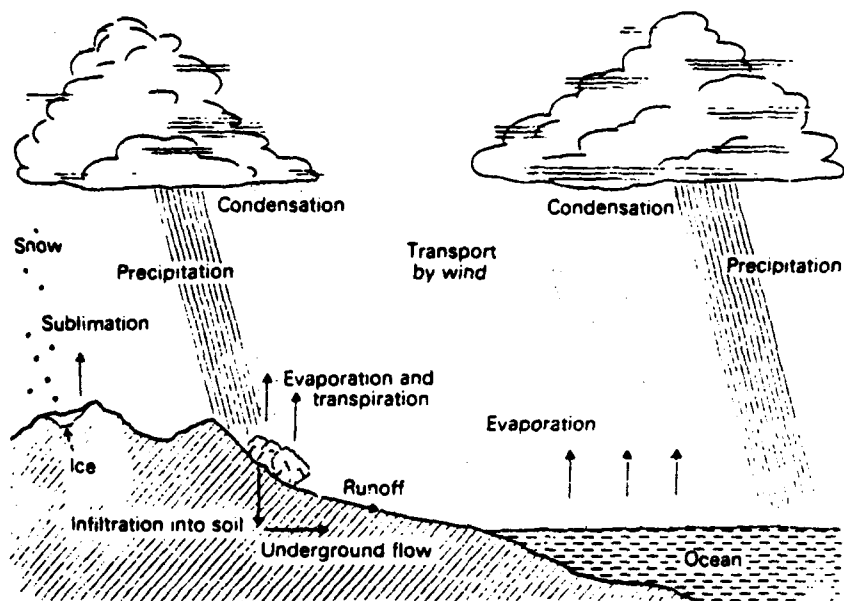


Figure 8. Schematic Representation of the Hydrologic Cycle

Source: Domenico, P.A., Concepts and Models in Groundwater Hydrology, McGraw-Hill Book Company, © 1972.

When enough water condenses in the atmosphere to form clouds, the water will fall to the earth as precipitation. Precipitation is the part of the hydrologic cycle which moves water from the atmosphere to the earth's surface. Generally, water stays in the atmosphere for 10 to 14 days before it falls to the earth's surface. (Table 6). Less than 0.01 percent of the earth's water is in the air at any given time.

Water on the surface of the earth is found in the oceans and on the land. Water in the oceans will remain there until it is circulated back to the atmosphere through vaporization. The principal way in which water on the land surface is moved is via river flow. The term runoff applies to all water which is contributing to stream channel flow. There are two sources for runoff: overland flow and groundwater. Figure 9 (Davis and DeWiest, 1966) illustrates runoff.

Typically, as rain falls to the land surface, some is evaporated directly back to the atmosphere. Some of the precipitation will be intercepted by vegetation and will never reach the land surface. That which does reach the land will begin to infiltrate the soil and to be stored in surface depressions. When the soil's storage capacity has been reached and the surface depressions have been filled, the remaining volume of precipitation will begin to flow across the land in sheets. This is overland flow. The amount of overland flow which results from precipitation is a function of precipitation intensity, permeability of the ground surface, duration of precipitation, type of vegetation, area of drainage basin, distribution of precipitation, stream channel geometry, depth to water table, and slope of the surface. The overland flow which reaches river channels contributes to runoff. That which flows over the surface, but infiltrates the soil, or is stored in surface depressions before reaching a river, is not part of runoff.

Some of the water which exists below ground also contributes to surface runoff. Part of the infiltrate from precipitation will flow laterally at shallow depths to reach stream channels. Part will remain in the unsaturated soil. But some will also percolate down to the groundwater system and contribute to stream base flow.

The groundwater system is the subsurface component of the hydrologic cycle. Underground water moves downward due to gravity and flows laterally in response to potential gradients. It percolates through the pores of rock or soil, and through the cracks and joints of rocks which have very little porosity.

The groundwater system is typically broken down into components, as illustrated in Figure 10. The two major components to the system are the unsaturated vadose zone and the saturated phreatic zone. The vadose zone is further divided into the zone of soil moisture and the intermediate zone. The zone of soil water is the shallowest component of the groundwater system. It is distinguished from deeper unsaturated zones in that its water content is subject to large fluctuations due to evapotranspiration. The zone of gravitational water lies beneath the zone of soil water and is also unsaturated. This zone may be totally

TABLE 6. ESTIMATE OF THE WATER BALANCE OF THE WORLD

Parameter	Surface area (km ²) × 10 ⁶	Volume (km ³) × 10 ⁶	Volume (%)	Equivalent depth (m)*	Residence time
Oceans and seas	361	1370	94	2500	~4000 years
Lakes and reservoirs	1.55	0.13	<0.01	0.25	~10 years
Swamps	<0.1	<0.01	<0.01	0.007	1-10 years
River channels	<0.1	<0.01	<0.01	0.003	~2 weeks
Soil moisture	130	0.07	<0.01	0.13	2 weeks-1 year
Groundwater	130	60	4	120	2 weeks-10,000 years
Icecaps and glaciers	17.8	30	2	60	10-1000 years
Atmospheric water	504	0.01	<0.01	0.025	~10 days
Biospheric water	<0.1	<0.01	<0.01	0.001	~1 week

*Computed as though storage were uniformly distributed over the entire surface of the earth

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

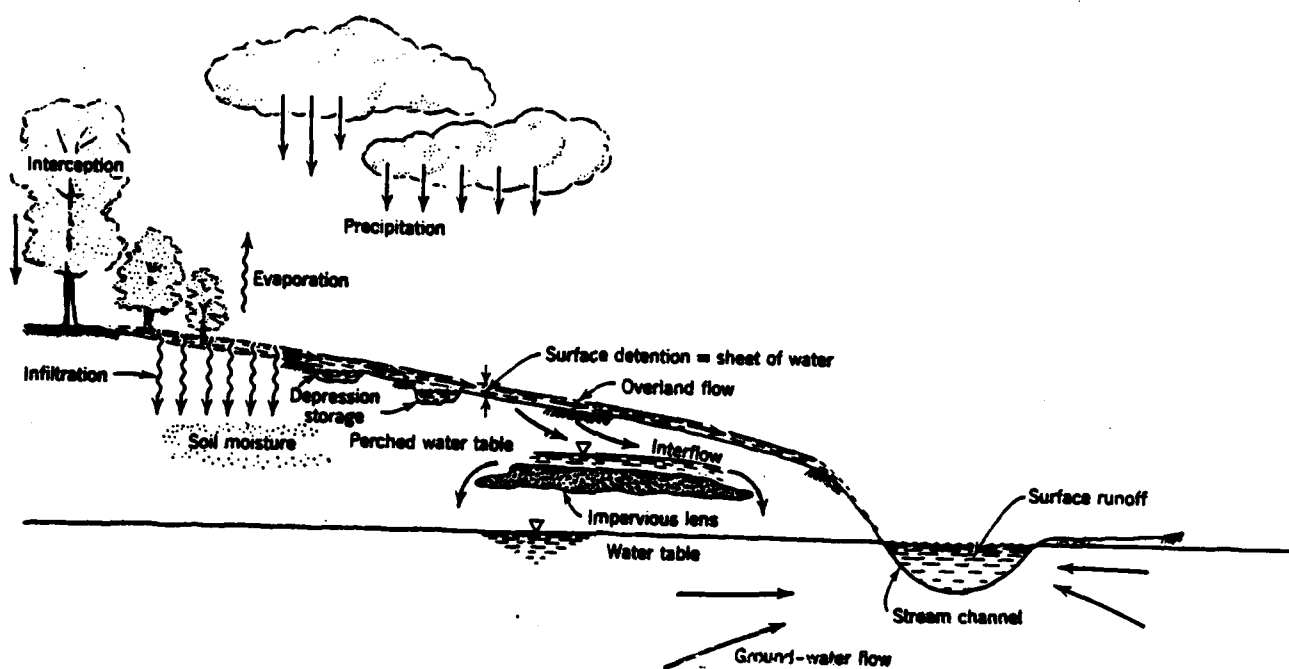


Figure 9. Simple Picture of a Runoff Cycle

Source: Davis, S.M. and R.J.M. DeWiest, . Hydrogeology, John Wiley and Sons, Inc., © 1966.

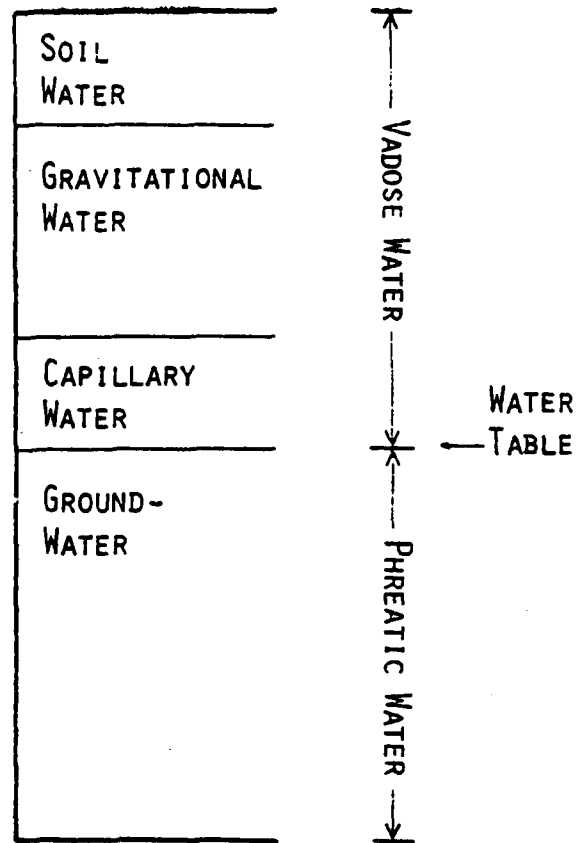


Figure 10. Classification of Subsurface Water.

Source: LeRoy, L.W. et al., Subsurface Geology -- Petroleum, Mining, Construction, Colorado School of Mines, 4th Edition, ©1977.

absent in humid regions or thousands of feet thick in arid regions. Water moving through the vadose zone may be found in two forms: hygroscopic water - moisture held to the soil particles, and gravitational water - water moving downward under the force of gravity.

Lying below the unsaturated zone is the phreatic zone. Phreatic water is defined as water that will freely enter wells. Like the vadose zone, the phreatic zone is broken down into two components. The capillary zone is a transitional zone between the unsaturated and saturated groundwater zones. In this zone water is held to soil or rock particles by surface tension. The capillary zone is saturated at the bottom, becoming less so upward. The water table terminates the capillary zone from below. The water table is a theoretical surface at which hydrostatic pressure equals atmospheric pressure. All water below the water table is groundwater. Groundwater occurs in four modes: hygroscopically, as water free to move in response to potential gradients, in unconnected pores, and in chemical combination with rock.

Groundwater is discharged to the surface naturally as stream base flow and through springs, and artificially, through manmade wells. It may also flow directly to the ocean, or be trapped in pore spaces within rock. Soil water is usually circulated to the atmosphere by transpiration. Evaporation is not usually a significant means of groundwater discharge, unless the water table is very near the surface or the soil is nearly saturated.

2. METEOROLOGICAL EFFECTS ON GROUNDWATER CONTAMINATION

Management of groundwater pollution incidents typically requires (1) definition of the extent of the contaminant zone; and (2) selection of a method to contain and/or treat the contaminant plume. The rate of future contaminant migration is among the governing factors in managing such incidents, and is a function of the recharge rate to the local groundwater system. Freeze and Cherry (1979) define groundwater recharge as "the entry into the saturated zone of water made available at the water table surface, together with the associated flow away from the water table within the saturated zone." The recharge rate to an aquifer depends on a number of factors including the available precipitation and temperature. These two parameters, precipitation and temperature, together with barometric pressure, wind velocity, humidity, and clouds define the condition of the earth's atmosphere, or weather. Meteorology is the study of the atmosphere, as it relates to predicting weather. This section addresses the effect that these meteorological factors, specifically precipitation and temperature, have on recharge and, hence, on the transport of groundwater contaminants.

Groundwater recharge rate is directly related to local precipitation. Precipitation and recharge will vary with overall climate, as well as seasonally. For example, in arid climates the depth to water is generally large. In more humid climates, the elevation of the water table tends to be shallower. As a result, pollutants in arid regions can accumulate in the unsaturated zone for a longer time, and be periodically released to the groundwater system. In humid areas,

contaminants often enter the saturated zone immediately and provide a steady source to the groundwater system.

Seasonal meteorological fluctuations are generally reflected hydrologically as fluctuations in the elevation of the water table, or the thickness of the unsaturated zone. In general, the water table is at its highest in late spring, and at its lowest at the end of winter. This is because temperature also affects recharge. For example, precipitation in the form of snow is not available to recharge the groundwater system until it has melted. Also, ice, clogging pore spaces in frozen soil slows or prevents infiltration. In areas of substantial irrigation, the water table is typically at its lowest in late fall at the end of the irrigation cycle.

Seasonal fluctuations in the thickness of the unsaturated zone and in the elevation of the water table can affect contaminant movement in a number of ways. Flow in the unsaturated zone is driven by gravity, and is typically downward only. The thickness of the unsaturated zone is a principal factor required for a contaminant to reach the water table and be entrained in lateral groundwater flow. This is an important factor in gauging contaminant migration. In the case of a spill of a soluble material, fluctuations in the water table could affect the prediction of the amount of time required for a contaminant to be entrained in the groundwater flow, and begin lateral movement. Insoluble contaminants which float on the top of the water table are particularly sensitive to fluctuations in water table elevation. According to the American Petroleum Institute (1972), "If the water table drops, oil will follow and some of it will be absorbed by the soil it passes through. When the water table rises, oil previously absorbed by the soil will be picked up and then continue to move laterally with the groundwater."

The continuity of aquifer recharge is another important consideration in characterizing the extent of contamination. Many localities receive regular rainfall resulting in fairly continuous aquifer recharge. However, at others, precipitation may be more variable, producing bursts of recharge instead. This pattern should not be neglected when estimating the direction of contamination movement, because plumes will reflect such variations. Figure 11 illustrates a hypothetical hydrological setting receiving periodic recharge. In a hydrologic investigation there, water level readings at P and Q indicated a head gradient from left to right. Water quality samples taken at P and Q indicated contaminant gradient from right to left due to the concentration gradient. This set of contradictory information might be resolved with the consideration that an opposite head gradient could be possible within the error range for the water level measurement. However, this would be an inaccurate assessment. Even regular water quality sampling for changes in concentration would not aid in planning further investigation because groundwater flows so slowly that changes would be discounted by the error range for the sampling apparatus. In this situation, historical precipitation would

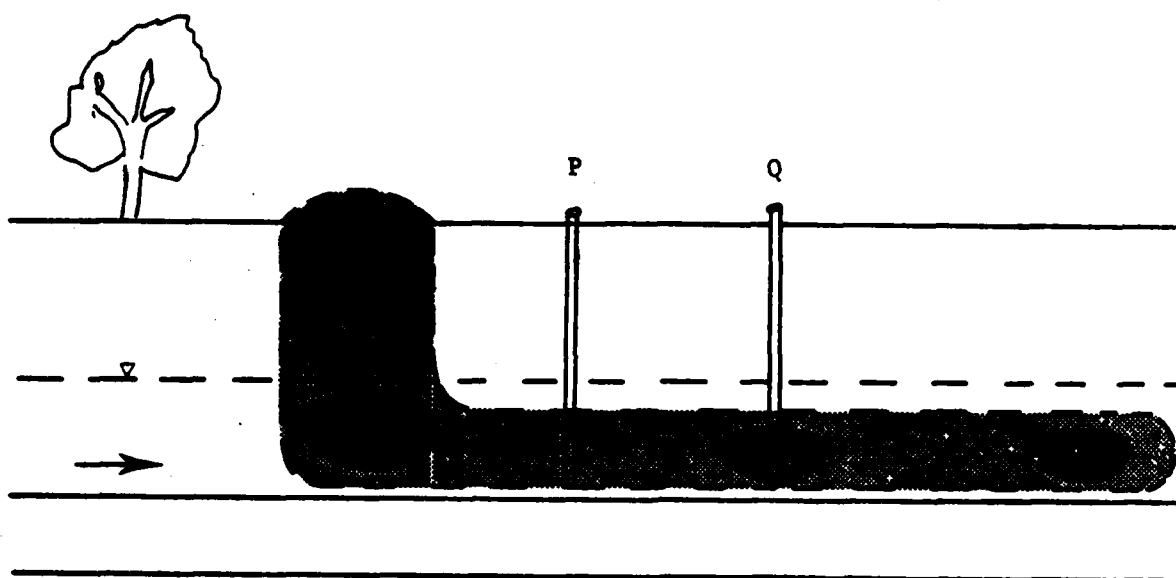


Figure 11. Effects of Periodic Recharge on Chemical Concentrations (Shading Darkness Reflects Concentrations)

be a key factor in characterizing the direction of contaminant migration.

Meteorological factors also affect the extent of aquifer contamination. Consider an example in which identical sampling programs are applied at two sites, one receiving periodic precipitation and one regular precipitation (Figure 12). Head gradient is the same at both sites. Wells A and B produce the same water quality data at both sites. In this example, an understanding of the recharge pattern is the key to accurately defining the extent of pollution at each site. Without this understanding, the extent of contamination could be underestimated, resulting in a misdirected control program.

Finally, recharge patterns are also important in analyzing the terminus of a contaminant plume. Historical precipitation data can indicate whether a higher quality sample at a contaminated site is the front of a plume or merely a hiatus in recharge. Similarly, higher water quality measured on the source side of the plume could be caused by diminished contaminant source or diminished recharge to transport the contaminant.

3. GEOLOGICAL EFFECTS ON GROUNDWATER CONTAMINATION

The movement of contaminated groundwater is controlled by physical and geochemical properties of (1) the contaminant; (2) the groundwater; and (3) the geologic system through which the contaminated groundwater is flowing. The lithology, stratigraphy, and structure of a region control the distribution of aquifers and confining beds, and affect the direction and rate of groundwater and contaminant migration. This section addresses the ways in which geologic factors affect the movement of contaminated groundwater. It begins with a discussion of the porosity and permeability of different rock types, and is followed by a discussion of how those hydrologic properties govern the groundwater pathway within a local geologic system.

The properties which control groundwater flow are porosity and permeability. Flint and Skinner (1974) describe porosity and permeability as they relate to groundwater movement:

"The limiting amount of water that can be contained within a given volume of rock material depends on the porosity of the material; that is, the proportion (in per cent) of the total volume of a given body of bedrock or regolith that consists of pore spaces (i.e., open spaces). So a very porous rock is a rock containing a comparatively large proportion of open space, regardless of the size of the spaces. Sediment is

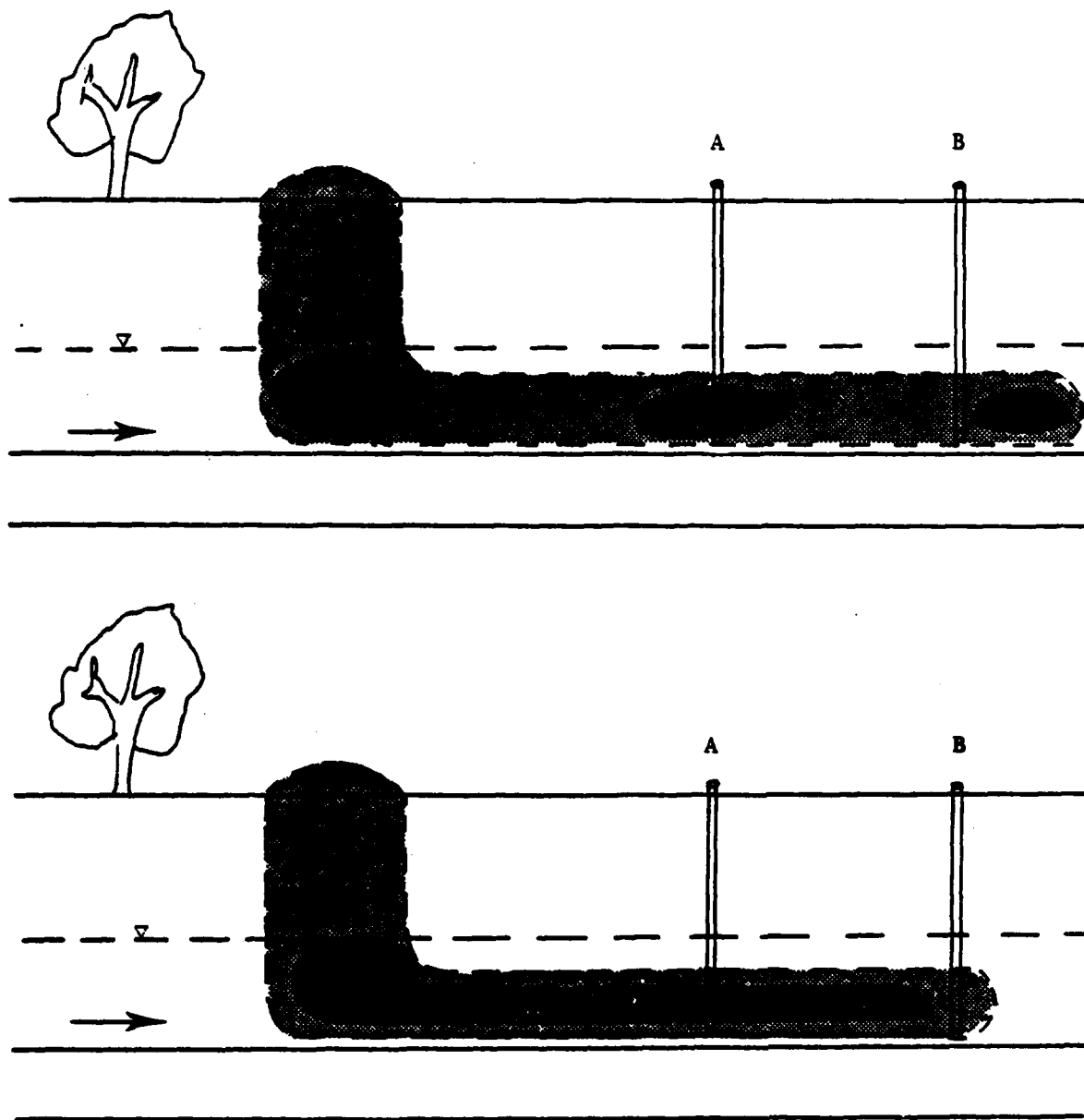


Figure 12. Periodic Versus Continuous Recharge
(Shading Darkness Reflects Concentration)

ordinarily very porous, ranging from 20 per cent or so in some sands and gravels to as much as 50 per cent in some clays. The sizes and shapes of the constituent particles and the compactness of their arrangement affect porosity, as does the degree, in a sedimentary rock, to which pores have become filled with cementing substances."

The porosity which results directly from the soil or rock matrix is termed primary porosity. The primary porosity of a rock unit may be enhanced by structurally controlled fracturing or dissolution, and this additional porosity is referred to as secondary porosity. Secondary porosity is usually the principal source of porosity in crystalline rocks. Flint and Skinner note that "igneous and metamorphic rocks generally have low porosity, except where joints and cracks have developed in them." Table 7 provides some representative ranges of porosity values typically exhibited by various geologic media.

High porosity in a rock unit does not necessarily result in groundwater movement. Only a combination of favorable porosity and favorable permeability will permit groundwater flow.

"Permeability is capacity for transmitting fluids. A rock of very low porosity is likely also to have low permeability. However, high porosity values do not necessarily mean high permeability values, because size and continuity of the openings influence permeability in an important way. The relationship between size of openings and the molecular attraction of rock surfaces plays a large part. Molecular attraction is the force that makes a thin film of water adhere to a rock surface despite the force of gravity; an example is the wet film on a pebble that has been dipped in water. If the open space between two adjacent particles in a rock is small enough, the films of water that adhere to the particles will come into contact. This means the force of molecular attraction is extending right across the open space, as shown on the left side of Figure 3-6. At ordinary pressure, therefore, the water is held firmly in place and so permeability is low. This is what happens in a wet sponge before it is squeezed. The same thing happens in clay, whose particles are so tiny their diameters are less than 0.005 mm.

By contrast, in a sediment with grains at least as large as sand grains (0.06mm to 2mm) the open

TABLE 7. RANGE OF VALUES OF POROSITY (N)

	<i>n</i> (%)
Unconsolidated deposits	
Gravel	25-40
Sand	25-50
Silt	35-50
Clay	40-70
Rocks	
Fractured basalt	5-50
Karst limestone	5-50
Sandstone	5-30
Limestone, dolomite	0-20
Shale	0-10
Fractured crystalline rock	0-10
Dense crystalline rock	0-5

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc. © 1979.

spaces are wider than the films of water adhering to the grains. Therefore the force of molecular attraction does not extend across them effectively, and the water in the centers of the openings is free to move in response to gravity or other forces, as shown in Figure 13. This particular sediment is therefore permeable. As the diameters of the openings increase, permeability increases. With its very large openings, gravel is more permeable than sand and yields large volumes of water to wells." Flint & Skinner (1974, p. 155).

The permeability ranges for various sediment and rock types are listed in Table 8.

The porosity and permeability of a rock unit is controlled by its lithology, geometry, and spatial variability. Individual rock types have characteristic lithologic properties, and, depending on depositional environment, characteristic structure and stratigraphy, which govern groundwater flow within them (Figure 14). For example, sandstones tend to have hydrologic characteristics which are good for transmitting groundwater. Porosity in sandstone depends directly upon the amount of cementation and degree of compaction. Unlithified sands have porosities of 30 - 50 percent. Because the sediments become more compacted with burial, porosity in sandstones will decrease with increasing depth. Sandstone permeability follows well-defined trends in relation to porosity (Figure 15). As porosity increases so does permeability. However, the distribution of permeability within a unit may vary, both laterally and vertically. These variations depend on bedding, depositional environment, and stratigraphy. A zone which may appear homogeneous upon visual inspection, may actually vary in permeability by one to two orders of magnitude locally. This anisotropic variability typically favors lateral groundwater flow parallel to bedding planes. However, with increasing cementation and compaction, secondary porosity in the form of fractures may play a major role. In this case, the trend for increased permeability along bedding planes changes to higher fracture permeability in the vertical direction.

Shales often form extensive confining beds, but frequently they occur as discontinuous lenses. Primary porosities in shales range from 0 - 10 percent, and, as a result, permeability is usually very low. Permeability values can be on the order of 10^{-12} cm² to 10^{-15} cm² reducing groundwater flow to centimeters per century. Secondary porosity in the form of hairline fractures can increase shale porosity significantly to produce permeabilities on the order of 10^{-7} - 10^{-8} cm².

Like sandstone, hydrologic properties of limestone vary with depth, due to compaction effects. Young limestone porosity values range from 20 - 50 percent, whereas older ones may have little, if any. Generally such unaltered limestone deposits are not major sources of groundwater.

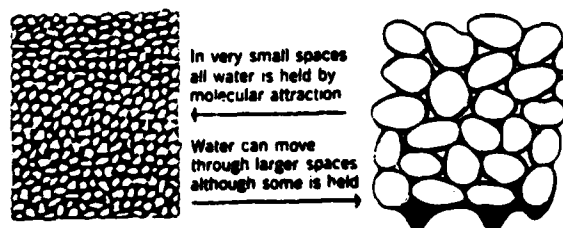


Figure 13. Effect of Molecular Attraction in the Intergranular Spaces in Fine Sediment (Left) and in Coarser Sediment (Right). Scale is Much larger than Natural Size.

Source: Flint, R.F. and B.J. Skinner, Physical Geology, John Wiley and Sons, Inc. © 1974.

TABLE 8. RANGE OF VALUES OF HYDRAULIC CONDUCTIVITY AND PERMEABILITY

Rocks	Unconsolidated deposits	k	k	K	K	K
		(darcy)	(cm ²)	(cm/s)	(m/s)	(gal/day/ft ²)
Karst limestone		10 ⁵	10 ⁻³	10 ²	1	10 ⁶
Permeable basalt		10 ⁴	10 ⁻⁴	10	10 ⁻¹	10 ⁵
Fractured igneous and metamorphic rocks		10 ³	10 ⁻⁵	1	10 ⁻²	10 ⁴
Limestone and dolomite		10 ²	10 ⁻⁶	10 ⁻¹	10 ⁻³	10 ³
Sandstone		10	10 ⁻⁷	10 ⁻²	10 ⁻⁴	10 ²
Unfractured metamorphic and igneous rocks		1	10 ⁻⁸	10 ⁻³	10 ⁻⁵	10
Shale		10 ⁻¹	10 ⁻⁹	10 ⁻⁴	10 ⁻⁶	1
Unweathered marine clay		10 ⁻²	10 ⁻¹⁰	10 ⁻⁵	10 ⁻⁷	10 ⁻¹
Glacial till		10 ⁻³	10 ⁻¹¹	10 ⁻⁶	10 ⁻⁸	10 ⁻²
Silt, loess		10 ⁻⁴	10 ⁻¹²	10 ⁻⁷	10 ⁻⁹	10 ⁻³
Silty sand		10 ⁻⁵	10 ⁻¹³	10 ⁻⁸	10 ⁻¹⁰	10 ⁻⁴
Clean sand		10 ⁻⁶	10 ⁻¹⁴	10 ⁻⁹	10 ⁻¹¹	10 ⁻⁵
Gravel		10 ⁻⁷	10 ⁻¹⁵	10 ⁻¹⁰	10 ⁻¹²	10 ⁻⁶
		10 ⁻⁸	10 ⁻¹⁶	10 ⁻¹¹	10 ⁻¹³	10 ⁻⁷

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

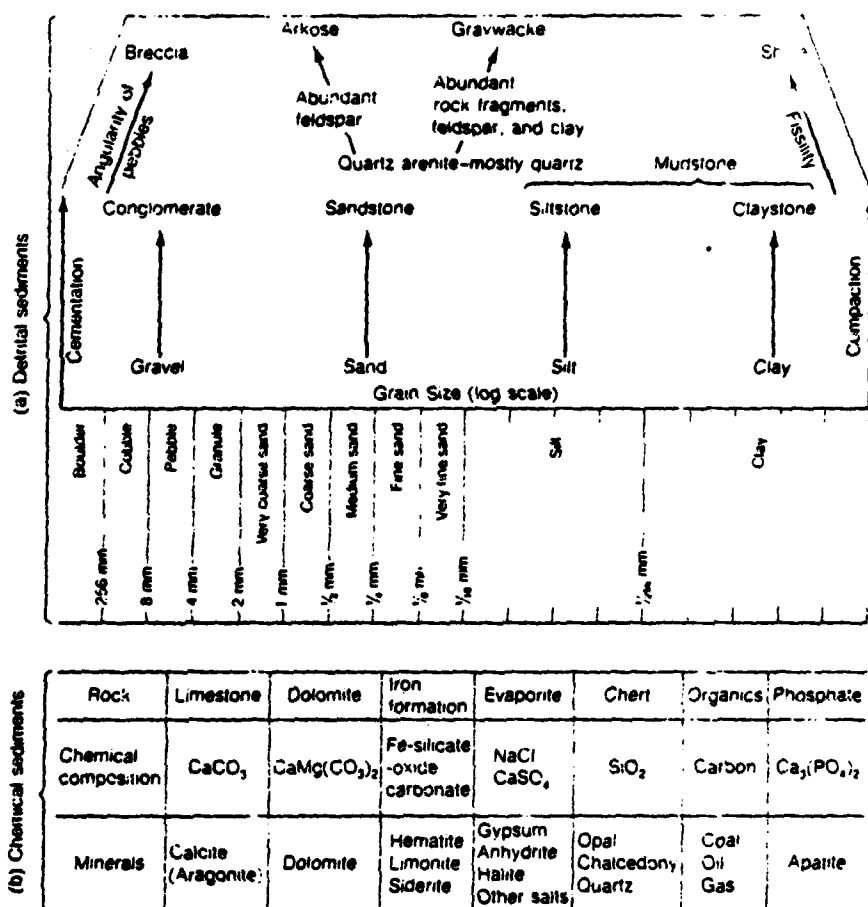


Figure 14. Sedimentary Rock Classification.
(a) Detrital Sediments. (b) Chemical Sediments.

Source: Press, F., and R. Siever, *Earth*, 2nd Edition, W.A. Freeman and Company, © 1978.

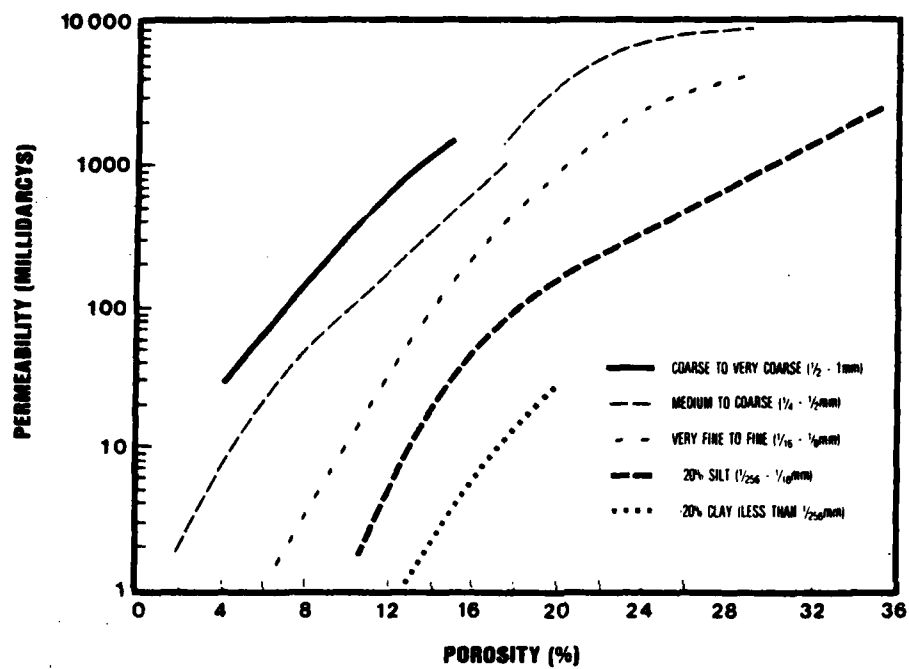


Figure 15. Relationship Between Porosity, Permeability, and Grain-Size Distribution of Sands and Sandstones.

Source: Adapted from Chilingar, Proc. Intern. Sedimentol. Congr., Amsterdam, Antwerp, 1963.

However, dolomitization, folding, and dissolution along fractures and in openings along bedding planes contribute to significant amounts of secondary porosity and permeability in these units.

Glacial drift is a special type of sedimentary deposit formed from continental glacial environments, and is the most abundant material that was deposited on the land surface during the Pleistocene. The lithology of a deposit can vary greatly. It can be sandy, with variable amounts of silt and minimal clay. This type of unit can form local aquifers. Others have high silt and clay content, with very little sand, resulting in a low permeability. Deposits of this type act as confining layers.

Plutonic igneous and unfractured metamorphic rock units have average primary porosities on the order of 2 percent. They can, however, develop significant secondary porosity resulting from fractures and dissolution. Fracture orientation may be vertical due to tectonic and thermal stresses or they may be horizontal, from overburden unloading. However, it is characteristic of crystalline rock for fracture permeability to decrease with depth. Extrusive igneous rocks, such as basalt can be more permeable from bubbles from entrapped gases, rubble zones from flow and differential solidification, interbeds of soils and stream channels, and columnar jointing from cooling. Extrusive igneous rocks tend to have dominantly lateral flow on a regional scale.

The course by which groundwater, and any accompanying contaminants travel to a discharge point is controlled by the rock units present in the hydrogeologic setting with water following the path of least resistance. Figure 16 from Freeze and Cherry (1979) illustrates some regional flow regimes which may result from various hypothetical hydrogeologic settings. Elements a through f are vertical cross-sections of identical dimensions. All cases represent a major valley running perpendicular to the page on the far left side of the system, with an upland valley to the right. Figure 16 illustrates a homogeneous system of a single rock type in which flow is effectively horizontal. In Figure 16, a higher permeability unit has been introduced below the original surface layer. This new layer exhibits essentially horizontal flow and is being recharged from above.

"If the hydraulic conductivity contrast is increased (Figure 16), the vertical gradients in the overlying aquitard are increased and the horizontal gradients in the aquifer are decreased. The quantity of flow is increased. One result of the increased flow is a larger discharge area, made necessary by the need for the large flows in the aquifer to escape to the surface as the influence of the left-hand boundary is felt.

In hummocky terrain (Figure 16) the presence of a basal aquifer creates a highway for flow

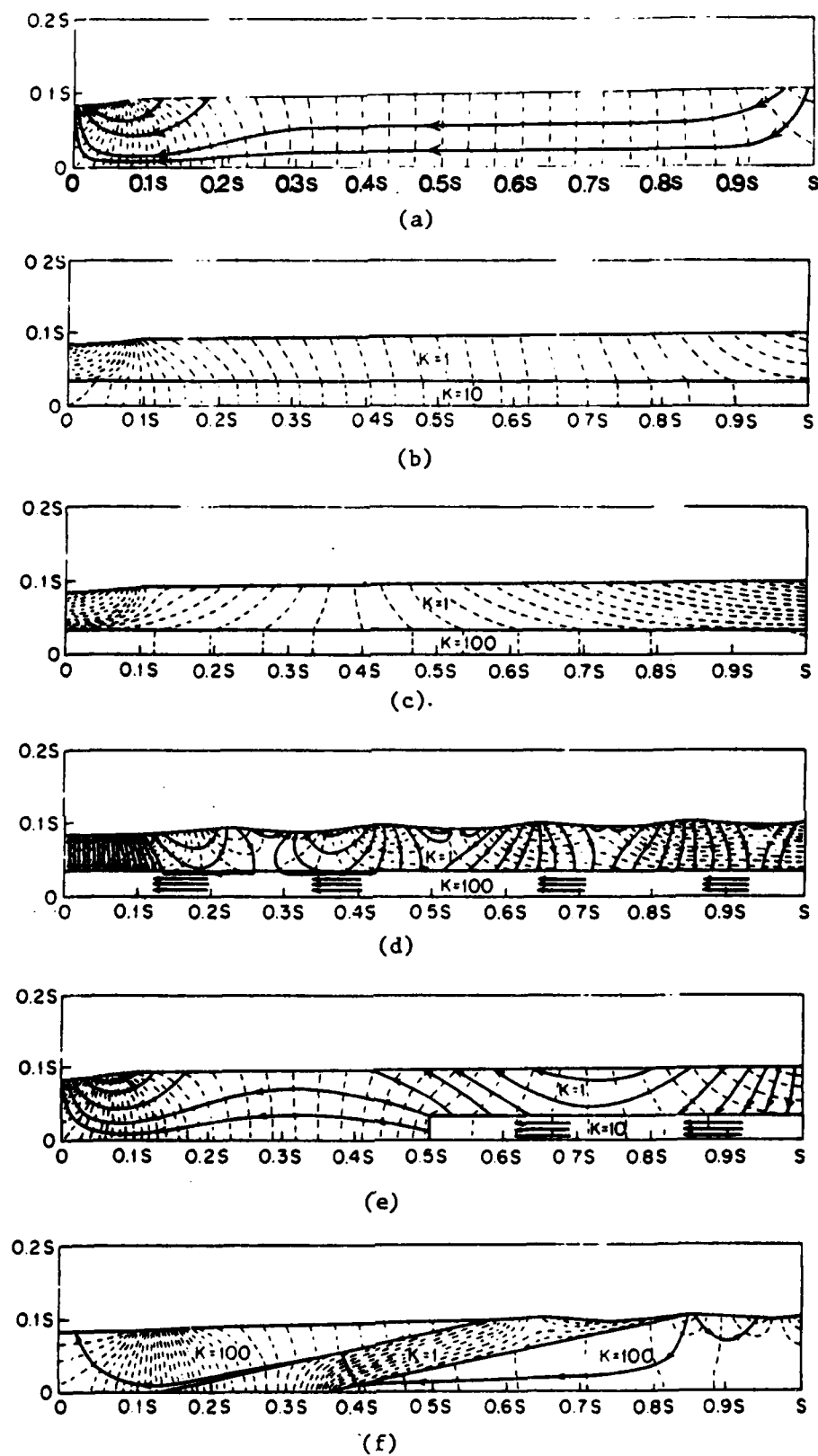


Figure 16 Effect of Geology on Regional Groundwater Flow Patterns.

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

that passes under the overlying local systems. The existence of a high permeability conduit thus promotes the possibility of regional systems even in areas of pronounced local relief.

There is a particular importance to the position within the basin of buried lenticular bodies of high conductivity. The presence of a partial basal aquifer in the upstream half of the basin (Figure 16) results in a discharge area that occurs in the middle of the uniform upland slope above the stratigraphic pinchout. Such a discharge area cannot occur under purely topographic control. If the partial basal aquifer occurs in the downstream half of the system, the central discharge area will not exist; in fact, recharge in that area will be concentrated.

In the complex topographic and geologic system shown in Figure 16, the two flowlines illustrate how the difference of just a few meters in the point of recharge can make the difference between recharge water entering a minor local system or a major regional system. Such situations have disturbing implications for the siting of waste disposal projects that may introduce contaminants into the subsurface flow regime." Freeze & Cherry (1979, p. 197).

The actual positioning of rock units in a region is determined from depositional environment, stratigraphy, and structural history. For example, glaciers advance and retreat leaving outwash plains of till and stream-deposited sand. Lakes dry up and lacustrine clay lenses are deposited. Marine shorelines transgress and regress leaving sands, shales and limestones that interfinger, pinch out, grade in and out of each other. Faulting disconnects continuous layers, positioning sand units abutting shales. All of those processes come together in a region to control a groundwater pathway. The variety of settings is almost infinite, and no two sites are precisely the same.

Figures 17 to 32 illustrate some hypothetical hydrogeologic landfill settings. They are only schematic, with simplified geology and hydrology, and they illustrate leachate flow principles in a general way only. They have been included as additional examples of how geology can affect contaminant migration (USEPA, 1980b).

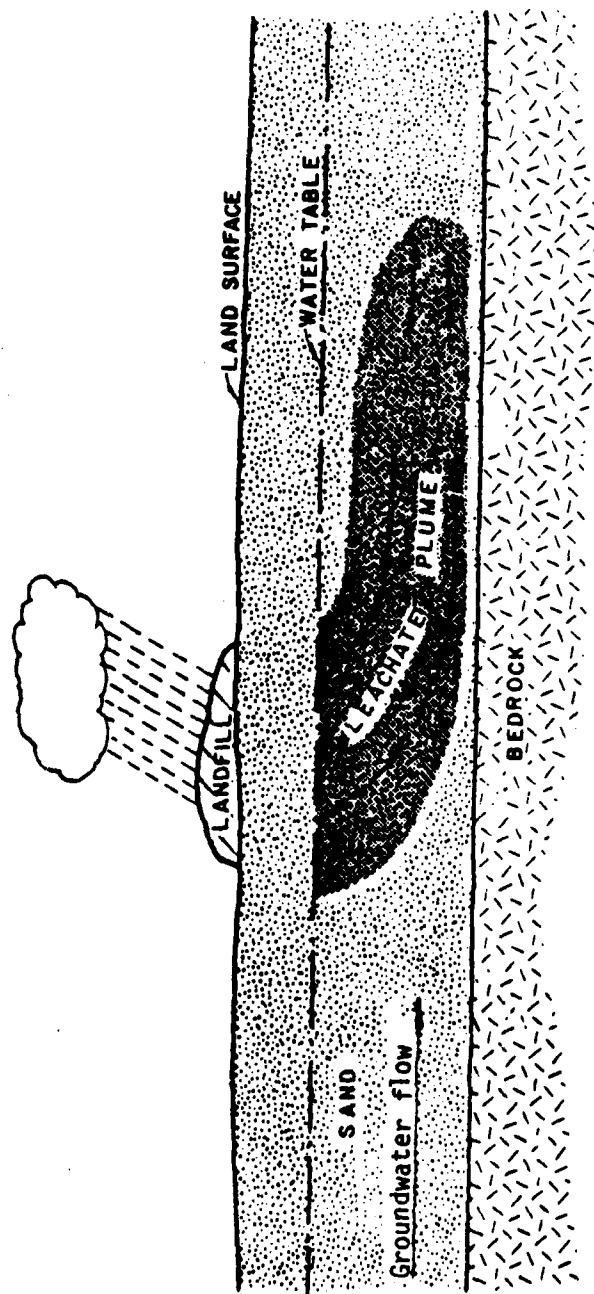


Figure 17. Single Aquifer With A Deep Water Table: Leachate percolates downward from the landfill to the underlying aquifer and then moves downgradient as a bulb or plume in the direction of groundwater flow. The mass of leachate may: 1) Sink to the bottom of the aquifer if of a heavier specific gravity, or 2) float at or near the top of the water-bearing unit if the leachate is predominately hydrocarbon in nature.

Source: EPA, 1980b.

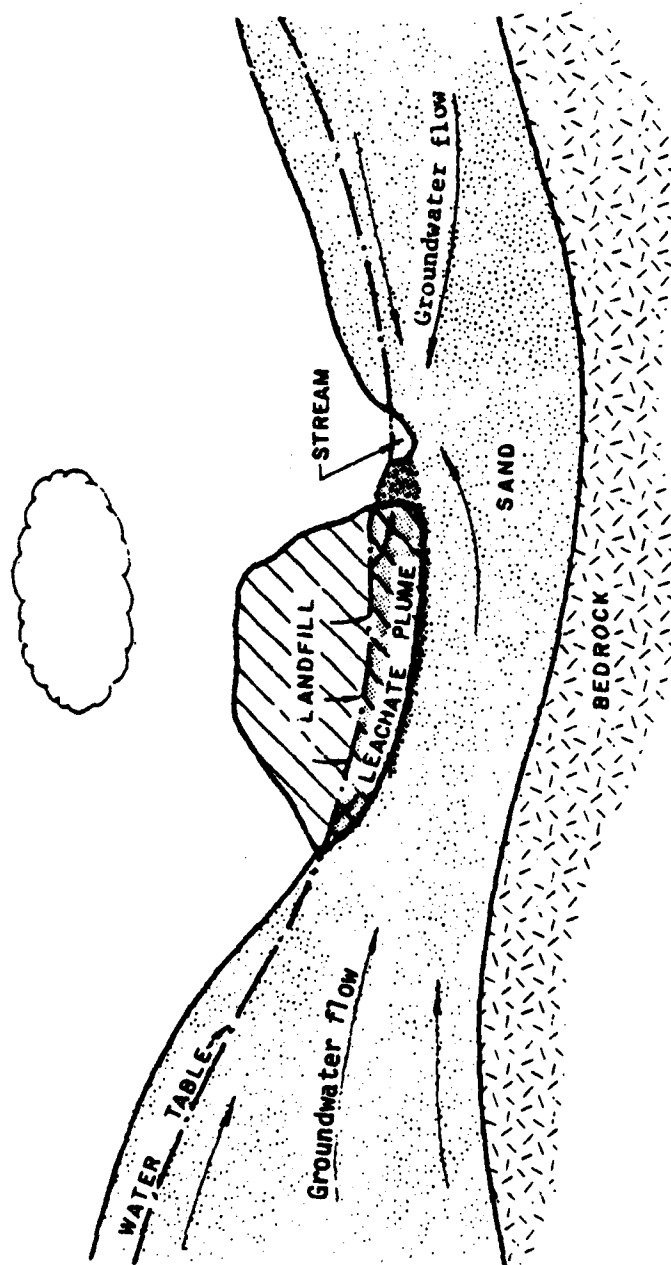


Figure 18. Groundwater Discharge Areas: Landfills located within the zone of saturation area always in contact with ground water moving from topographically higher recharge areas to a stream discharge point. In such cases, leachate is transported with the ground water to the stream where it becomes diluted by surface water.

Source: EPA, 1980b.

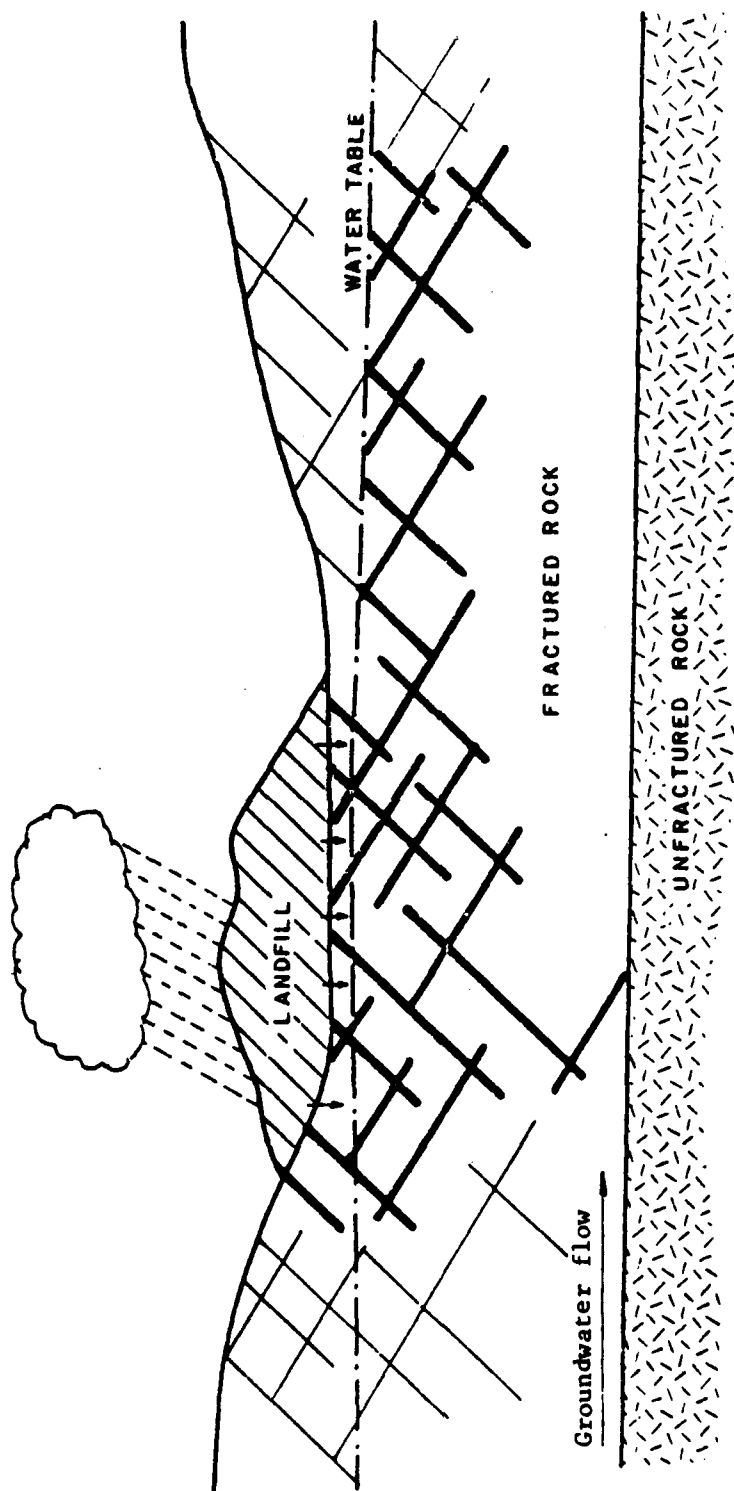


Figure 19. Fractured Rock Surface With A High Water Table: Leachate migrates downgradient along interconnected rock fractures to some lower natural discharge area or a pumping well.

Source: EPA, 1980b.

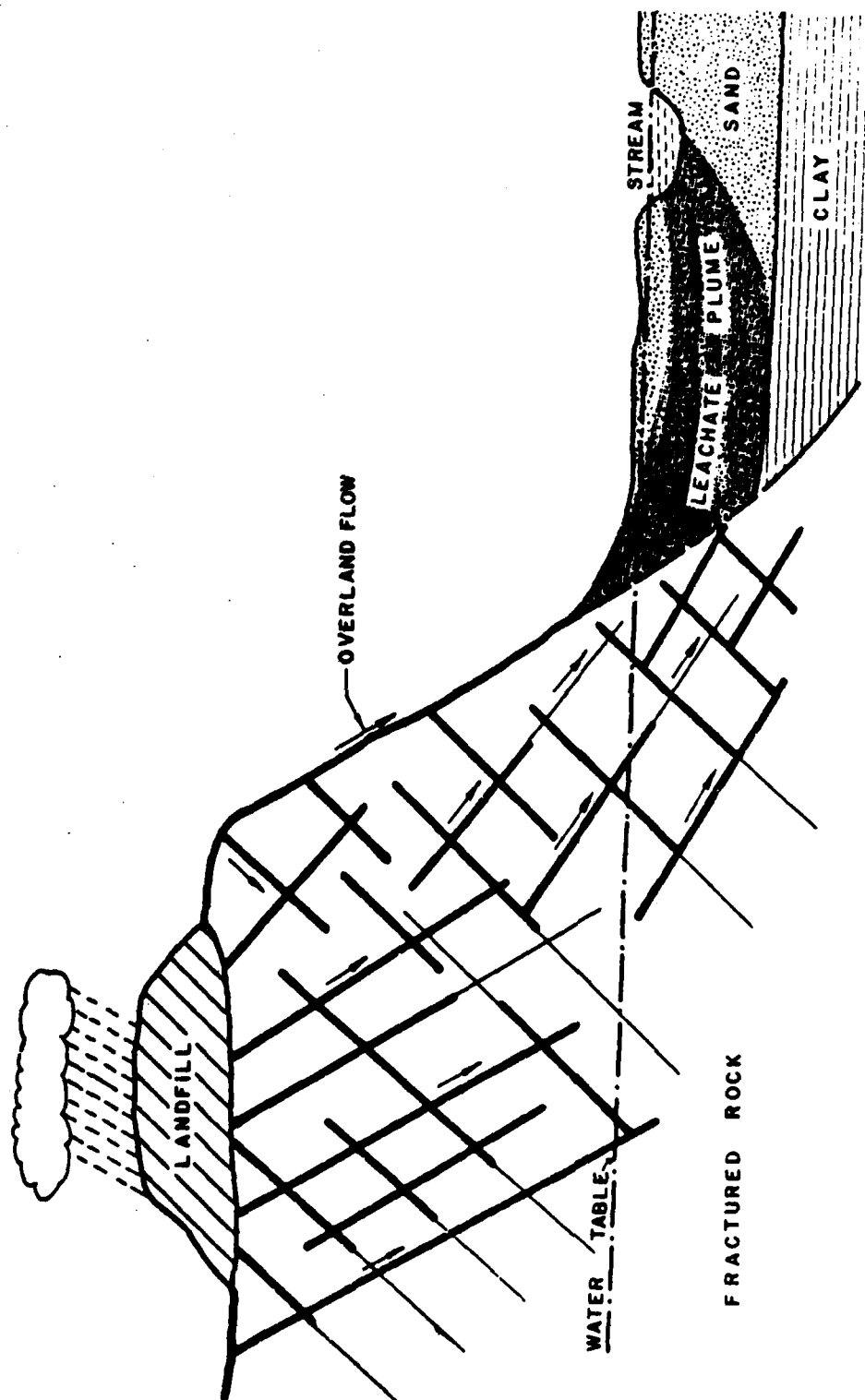


Figure 20. Fractured Rock Surface With a Deep Water Table: Leachate flows into and through interconnecting fractures and discharges either at the surface or into the subsurface where it moves with the groundwater to some more distant discharge point.

Source: EPA, 1980b.

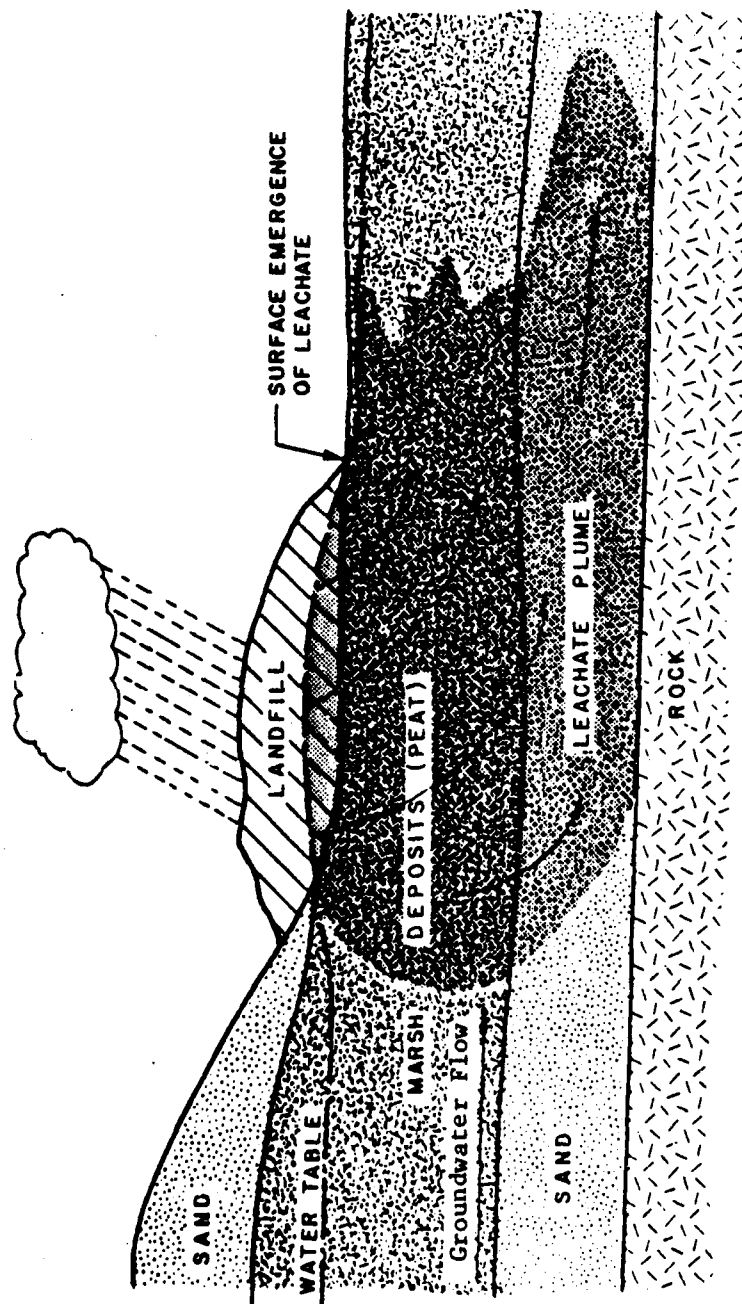


Figure 21. Marsh Deposit Underlain By An Aquifer: The water table is high, and a mound is formed at the base of the landfill. Leachate migrates downward through the marsh material to the aquifer. In many cases, surface emergence of leachate will occur at the toe of slope. Some contaminants may be attenuated within the marsh deposits. The portion reaching the water table moves through the aquifer with the groundwater to some surface discharge point.

Source: EPA 1980b.

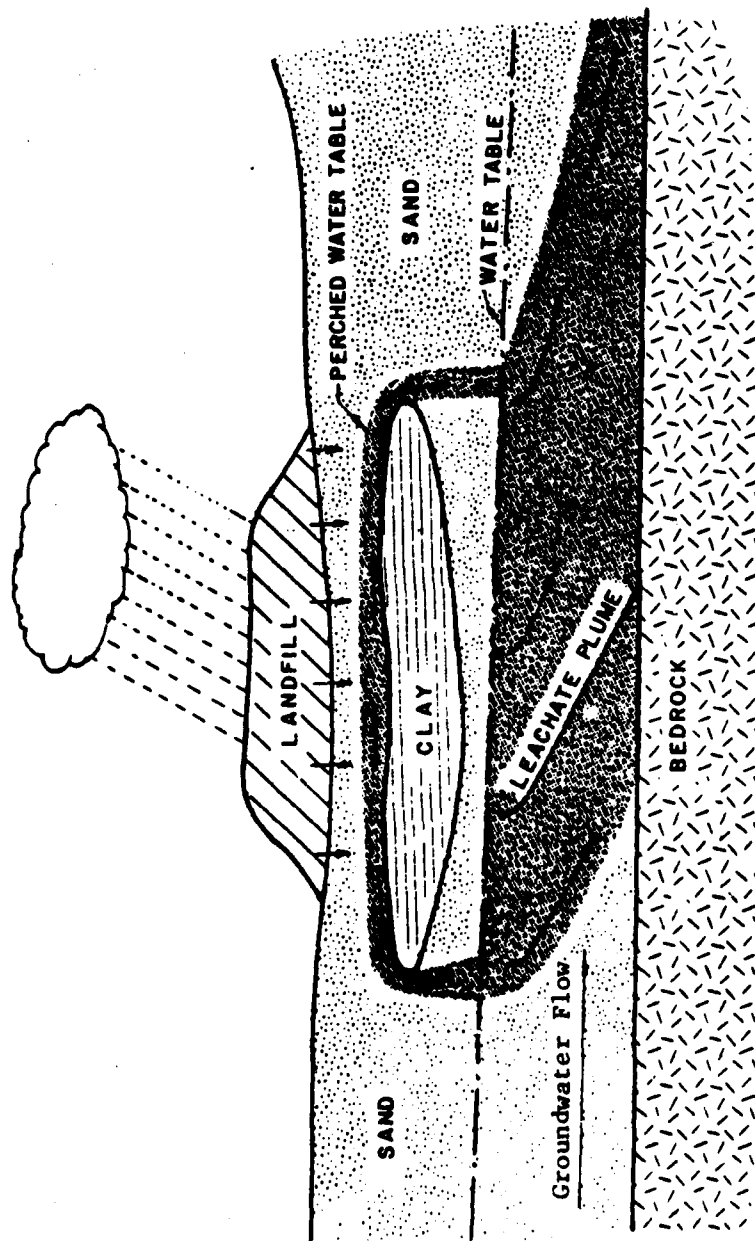


Figure 22. Permeable Sand Layer Underlain by a Clay Layer: The Water Table is Deep. Leachate Percolates Downward Under the Landfill, Forming a Perched Water Table Before Finally Reaching the Actual Water Table

Source: EPA, 1980b.

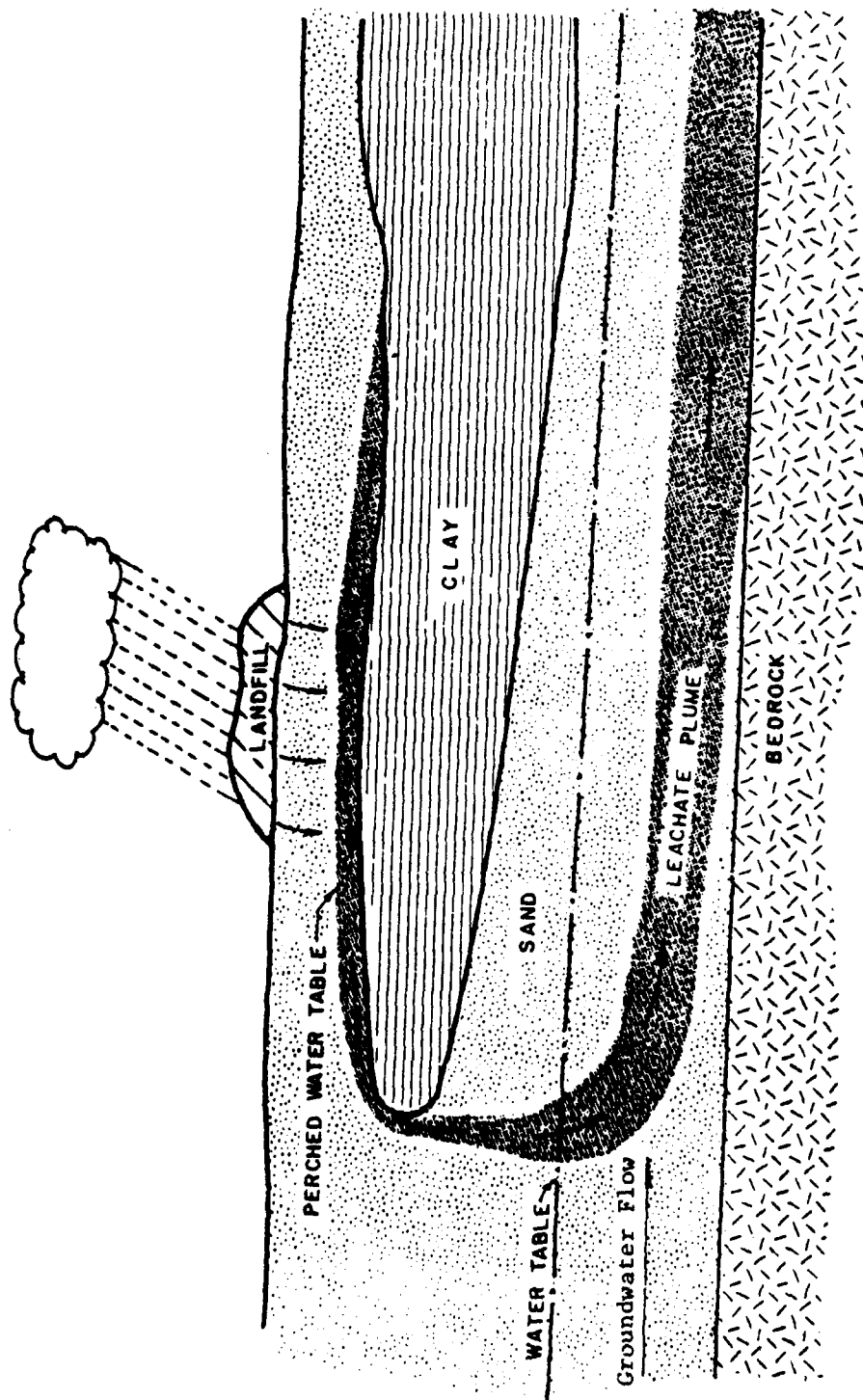


Figure 23. Perched Water Table Condition: Leachate Percolates to the Perched Water Table and Flows Downgradient to the end of the Confining Layer Where it Moves Downward to the Actual Water Table

Source: EPA, 1980b.

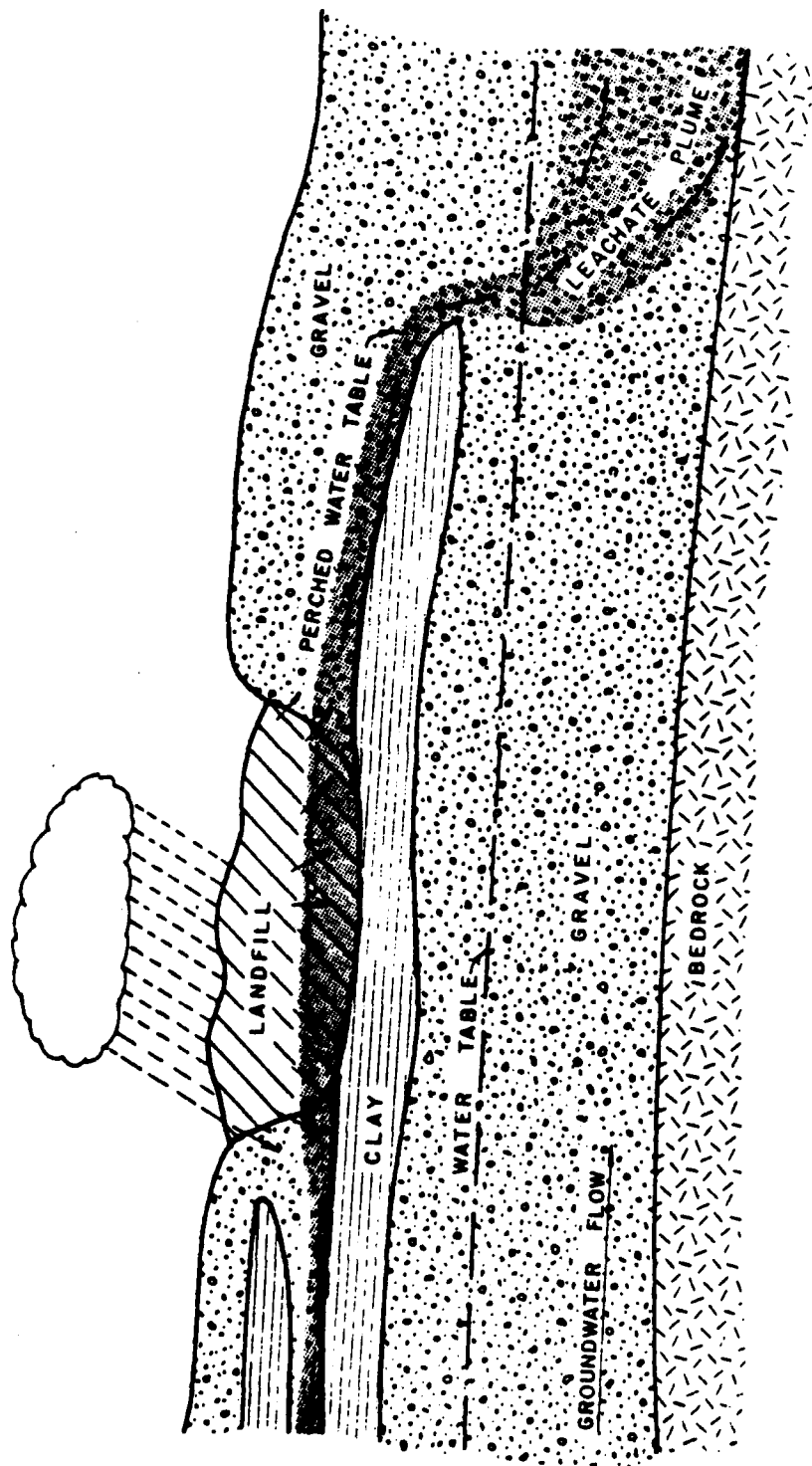


Figure 24. Abandoned Gravel Pit With A Clay Layer At Its Base: A perched water table (leachate) will build up under the landfill and flow laterally through the ground above the clay until it is free to percolate to the main water table.

Source: EPA, 1980 b.

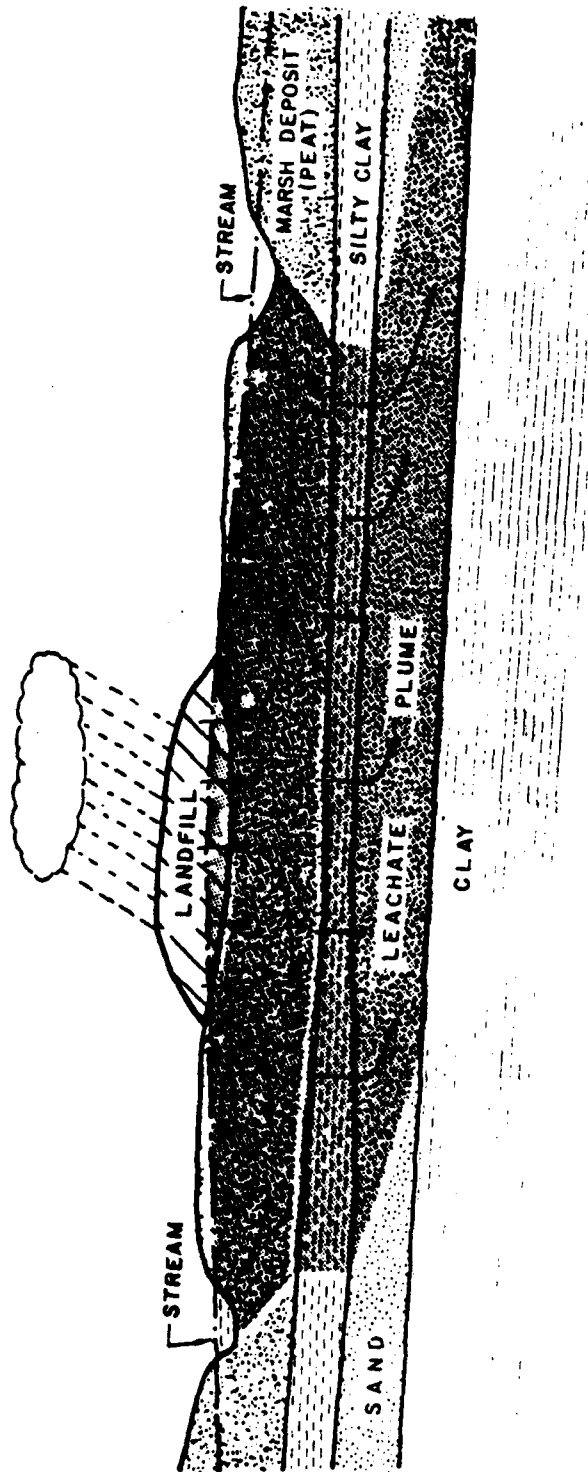


Figure 25. Marsh Deposits Bounded On Either Side By Streams and Underlain By a Shallow Aquifer: Leachate from the landfill may move horizontally through the marsh materials to the stream, or vertically downward as groundwater recharge to the aquifer.

Source: EPA, 1980b.

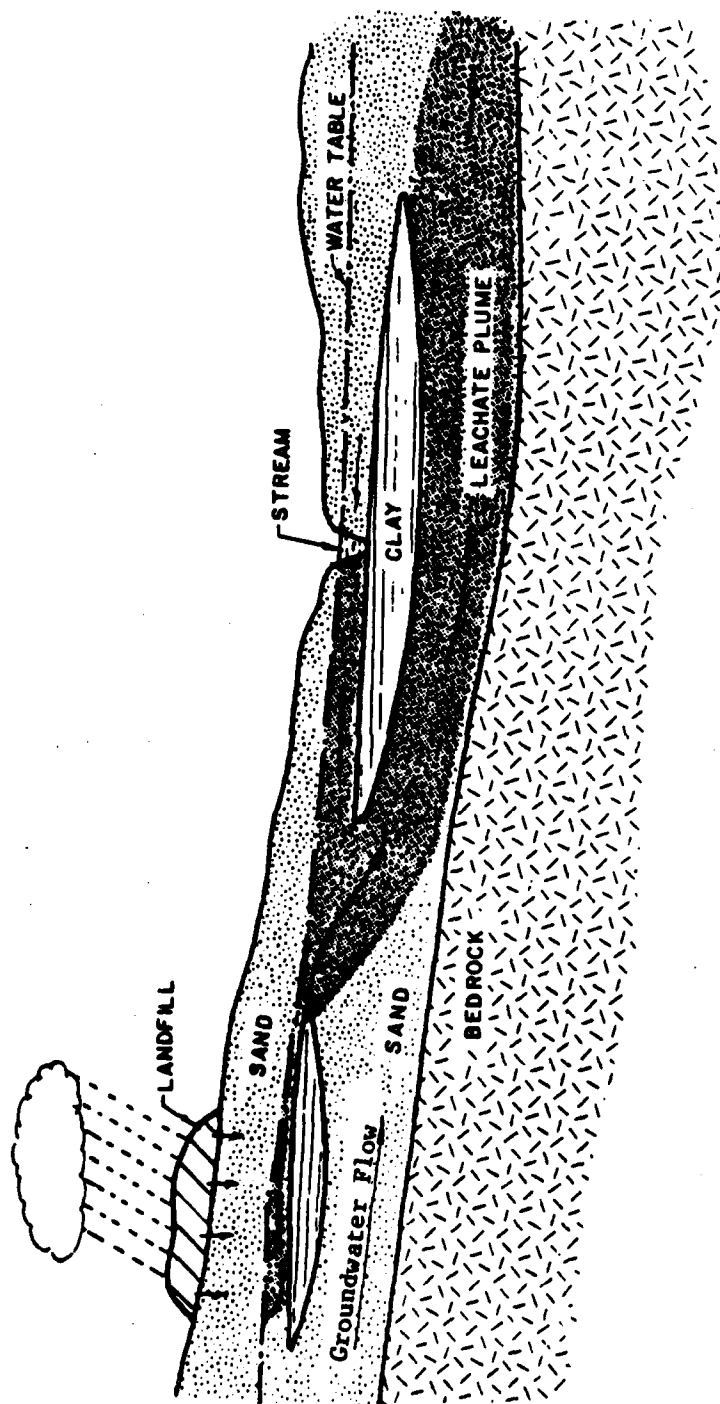


Figure 26. Single Aquifer Interbedded With Clay lenses: The leachate plume is split into two plumes by a clay lens. One plume discharges into a stream near the landfill while the other plume moves deeper into the aquifer and flows to a more distant discharge point.

Source: EPA, 1980b.

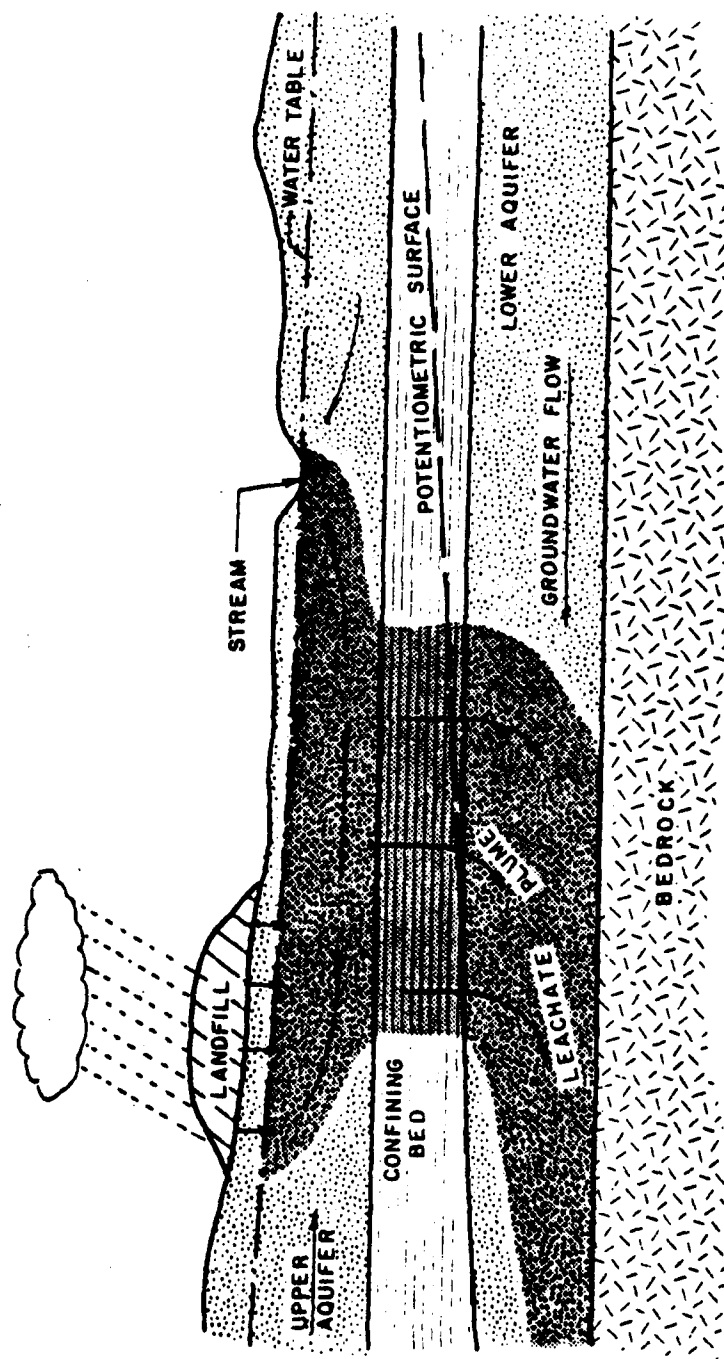


Figure 27. Two-Aquifer System With Opposite Flow Directions: Leachate first moves into and flows with the groundwater in the upper aquifer. Some of the leachate eventually moves through the confining bed into the lower aquifer where it flows back beneath the landfill and away in the other direction.

Source: EPA, 1980b.

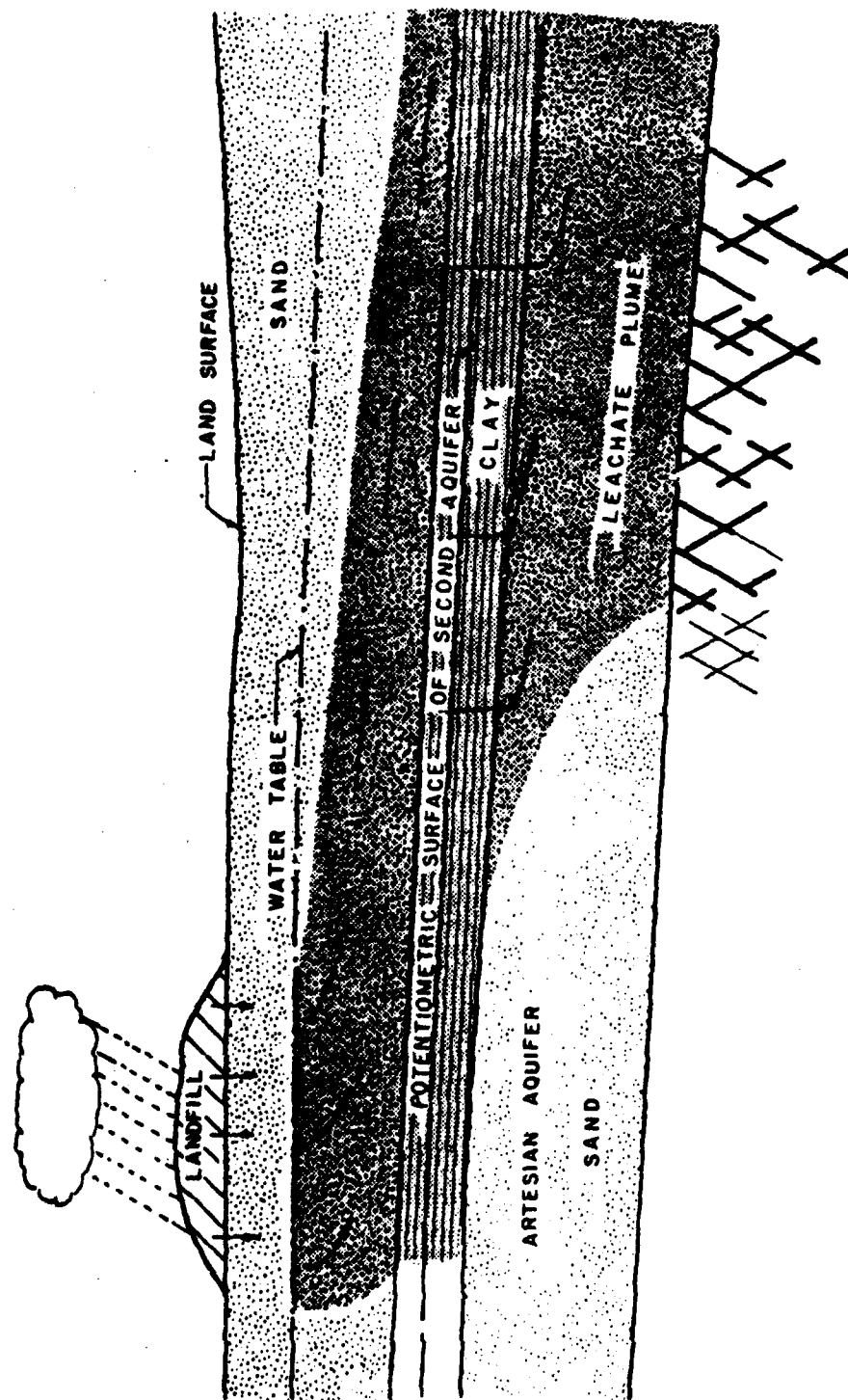


Figure 28. Three-Aquifer System With a Deep Water Table: Leachate percolates to the upper aquifer where it moves as a plume in the direction of groundwater flow. Eventually, some of the leachate moves through the confining layer and into the second aquifer that is interconnected with a fractured bedrock aquifer.

Source: EPA, 1980 b.

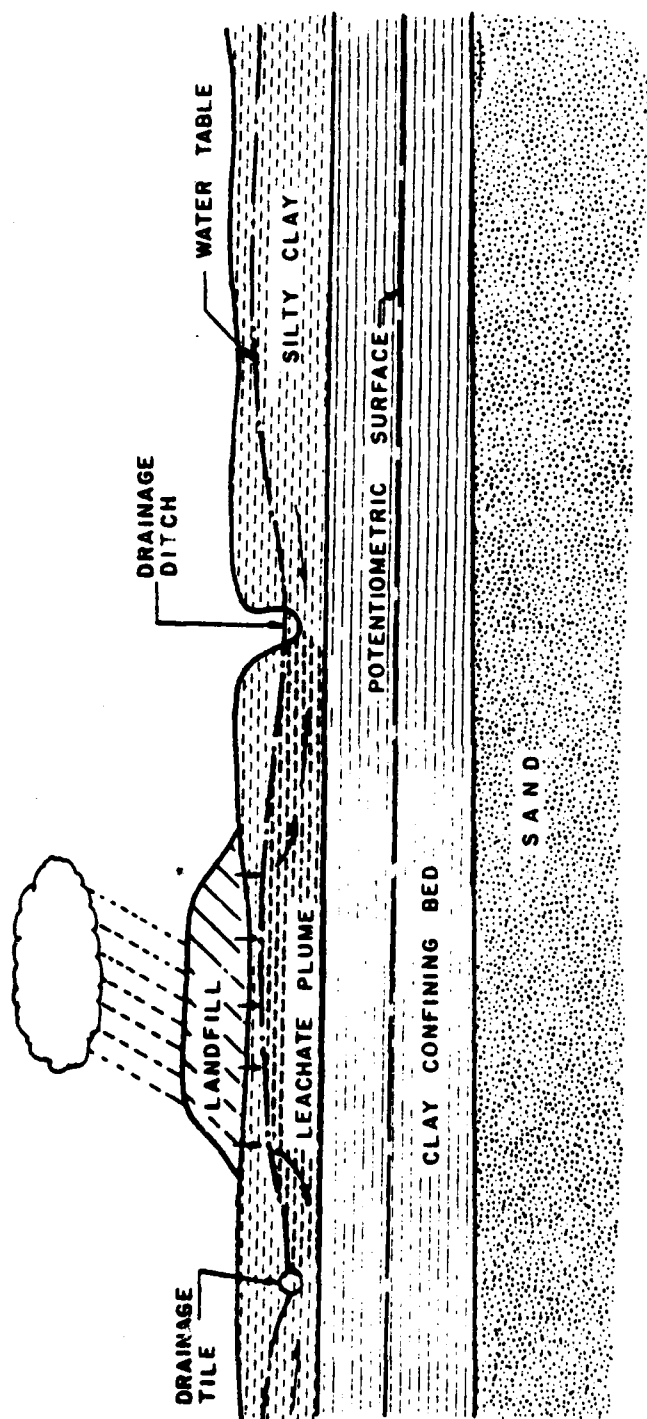


Figure 29. Thick Clay Layer Underlain By An Aquifer: Leachate is unable to penetrate the impermeable clay layer and discharges to the tile drainage systems or drainage ditches in the area around the landfill.

Source: EPA, 1980 b.

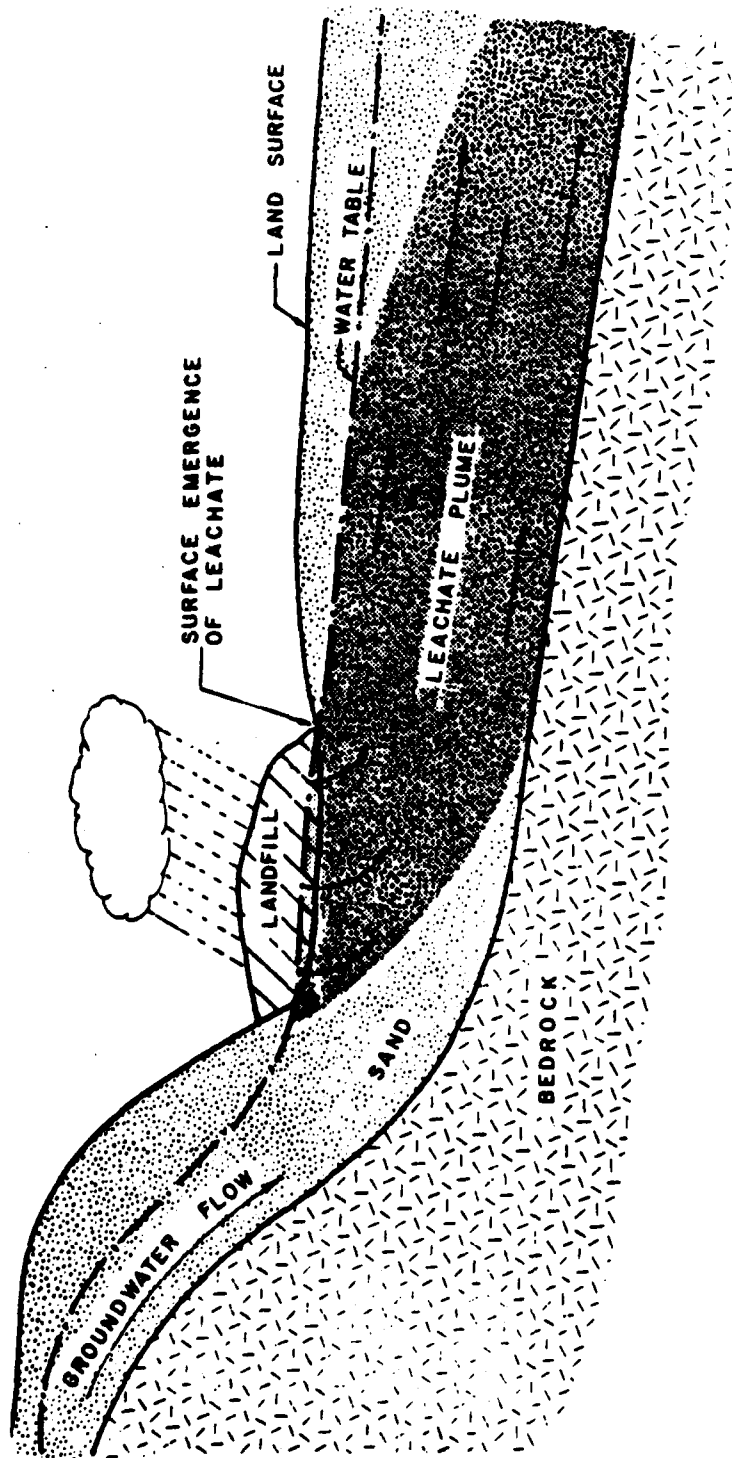


Figure 30. Single Aquifer Intersecting Landfill: A steep, shallow ground water table flows directly into the landfill, generating leachate which flows downward into the aquifer. Surface emergence of leachate may also occur.

Source: EPA, 1980 b.

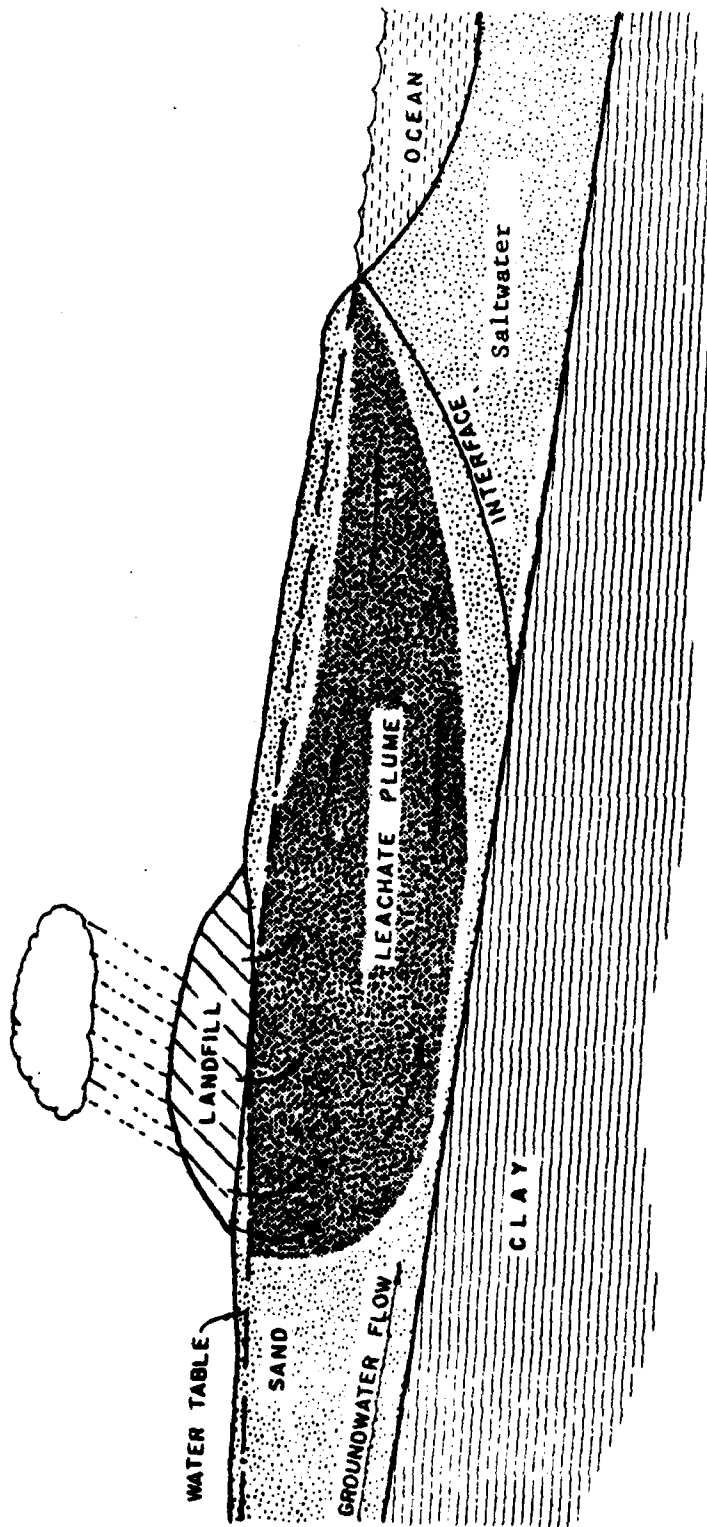


Figure 31. Landfill is Located Near Large Saltwater Body: The leachate plume flows down into the fresh-water aquifer and toward the open saltwater body. As the leachate plume reaches the fresh-salt interface, it is forced upward along the interface to discharge at or near the edge of the saltwater body.

Source: EPA, 1980b.

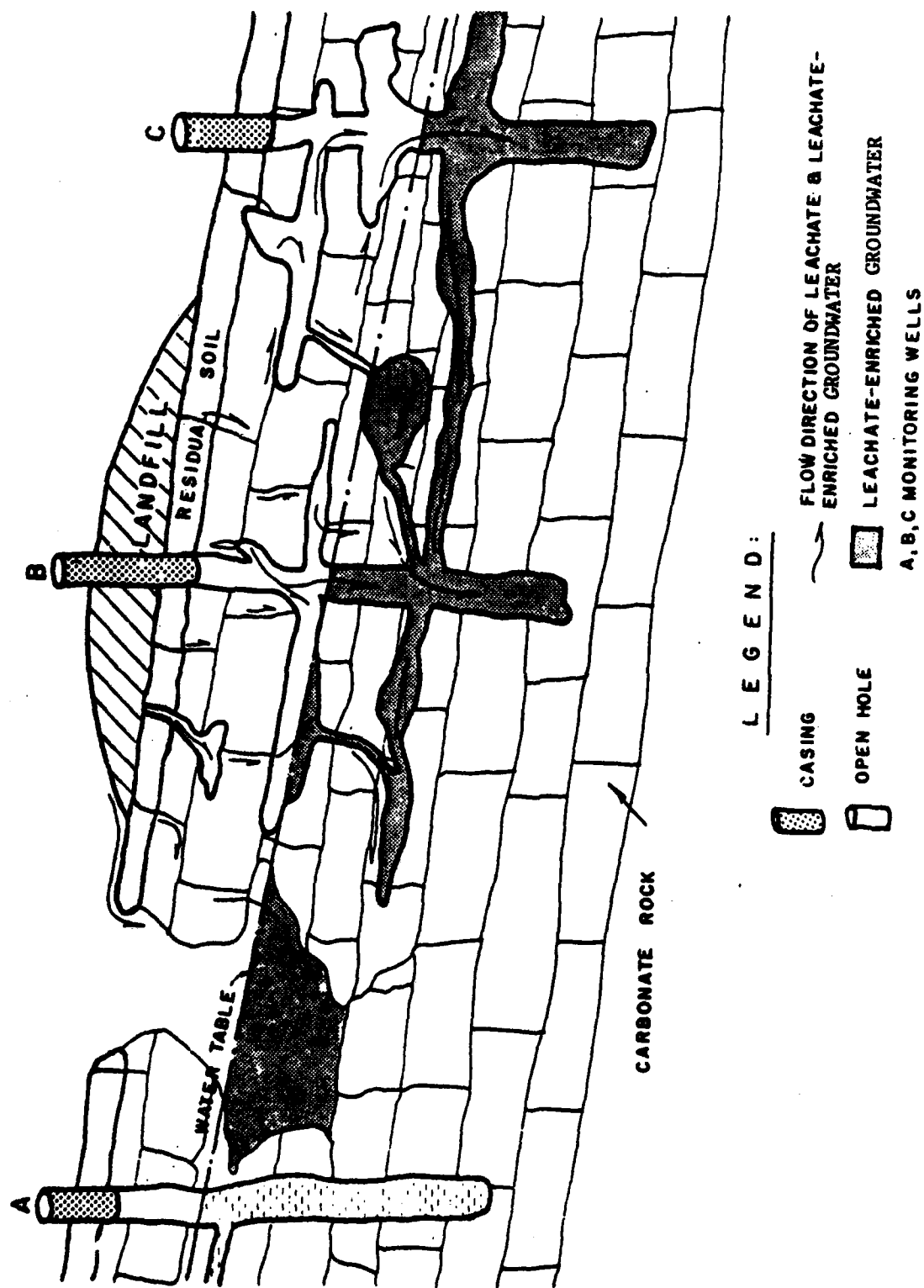


Figure 32. Monitoring Network For Aquifers With Solution Porosity-Vertical Flow
Source: EPA, 1980b.

4. EFFECTS OF PUMPING ON CONTAMINANT PLUMES

Under natural conditions groundwater flow systems are in a state of approximate dynamic equilibrium. Recharge to a system and discharges from it are in approximate balance when considered over a season or a climatic cycle. Human activities, including pumping water supply wells, recharge wells, or landfills, can affect a stable groundwater system. Such activities constitute stresses imposed on the system and must be balanced by changes in the pattern or amount of recharge to the system and discharge from the system by changes in the amount of water in storage, or by a combination of these. Such stresses also have impacts on the pathways and rates of migration of groundwater contaminants, since such stresses cause distortions of the equilibrium positions of equipotentials and streamlines.

In this section we are particularly concerned with the effects of pumping on the shape, location and migration of contaminant plumes. These pumping effects are of interest for two important reasons: (1) the potential for contamination of municipal or domestic water supply wells, and (2) the opportunities for manipulation of hydraulic gradients as a means of controlling migration of contaminants.

For the purposes of this discussion, and to clarify the important underlying principles, we will focus on a simplified physical situation consisting of a confined aquifer of infinite areal extent with uniform hydraulic properties and thickness.

Consider as a first case a flow regime consisting of a static horizontal potentiometric head profile (no gradients). On this regime, we superimpose the effects of a single pumping well. Figure 33 shows the streamlines and equipotentials which result. The configuration of streamlines (defining regions of equal flow) and equipotentials (contour lines of equal hydraulic potential) is referred to as a flow net. For this situation, the flow net shows flow occurring radially towards the well. Equipotentials consist of concentric circles of decreasing head as we move toward the pumping well. Darcy's law characterizes flow in a porous medium as the product of a proportionality constant, known as the hydraulic conductivity, and a gradient. By lowering the potential at a well, a potential difference, or gradient, is created between the well and adjacent materials, thus inducing flow towards the well. As a result the pumping stress leads to decreases in potential at points in the vicinity of the well. At a given point, the difference between the prepumping potential and the new lower potential resulting from pumping is called the drawdown. The new potentiometric surface is often referred to as the cone of depression, deriving its name from the shape of the surface of reduced potential observed around the well.

The shape of the cone of depression depends on the properties of the aquifer and the pumping rate. At any point at a given time drawdown is directly proportional to the pumping rate and inversely proportional to aquifer hydraulic properties. The aquifer properties of greatest importance are transmissivity, or the ability of an aquifer to transmit

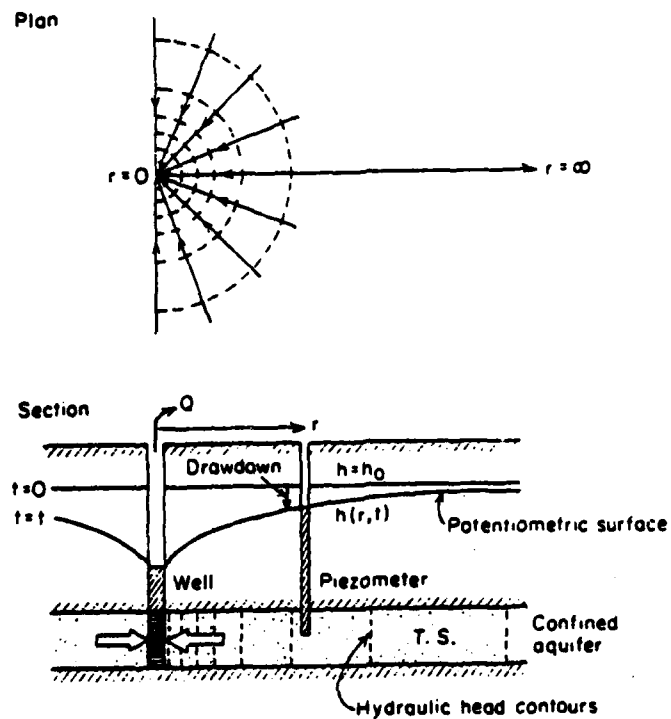


Figure 33. Radial Flow to a Well in a Horizontal Confined Aquifer

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

water, and storativity, or the ability of an aquifer to store water. Aquifers of high transmissivity develop shallow cones of depression of wide areal extent. Aquifers of low transmissivity develop deep cones of limited extent. Low storativity produces deeper drawdown than high storativity. It should be noted that for a given aquifer, the cone of depression increases in depth and extent with increasing time.

The discussion above is also valid for unconfined aquifers, although the physical situation is more complex. The storativity of an unconfined aquifer is referred to as the specific yield. Specific yields of unconfined aquifers are generally much higher than storativities of confined aquifers. Thus, cones of depression will be less extensive and shallower than for a confined aquifer with a similar transmissivity. In addition, pumping from an unconfined aquifer leads to actual dewatering of the aquifer, which is not the case for a confined aquifer. As a result, the thickness of the aquifer at any given point changes with time. This in turn affects the transmissivity of the aquifer. As Figure 34 indicates, flow lines toward a well in an unconfined aquifer are not horizontal, but have a vertical component, due to the variation in aquifer thickness induced by pumping. In a confined aquifer, thickness does not change and flow lines remain horizontal after imposition of a pumping stress. The practical result of these differences is that exact mathematical treatments of flow to a well in an unconfined aquifer are more complicated than treatments in a confined aquifer.

The preceding discussion assumed a static head profile as an initial condition in the aquifer. Water in an aquifer is actually moving in response to a gradient in potential. In other words, there is a slope to the potentiometric surface in a confined aquifer, and a slope to the water table in an unconfined aquifer. Furthermore, a velocity field characterizes the natural, prepumping conditions in an aquifer, on which the effects of a pumping well are superimposed.

Figure 35 shows the flow net and cone of depression for a well withdrawing water from an unconfined aquifer with an initially sloping water table. The flow is not radial towards the well, nor are the equipotentials concentric. This is a direct result of the previously existing flow conditions. We observe for this cone that there is a definite region of the aquifer upgradient from the well from which the well captures water. Outside this region, the streamlines do not terminate at the well, and water will flow past the well. This is in contrast to the static case where all streamlines terminate at the well.

The significance of this difference relates to the existence of an area of capture, from which the well draws. If a landfill, waste dump or other source of contamination exists within this area upgradient from a well, pollutants from the source can be expected to appear in the water derived from the well. Conversely, if a plume of contaminated water exists in an aquifer, it should be possible to install wells downgradient so as to intercept the plume.

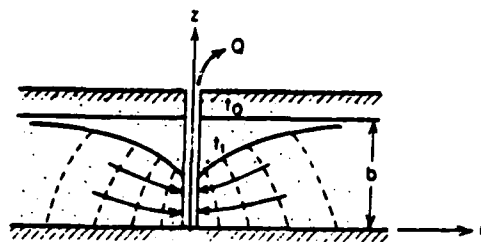


Figure 34. Radial Flow to a Well in an Unconfined Aquifer.

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

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GROUNDWATER CONTAMINATION RESPONSE GUIDE VOLUME 2 DESK

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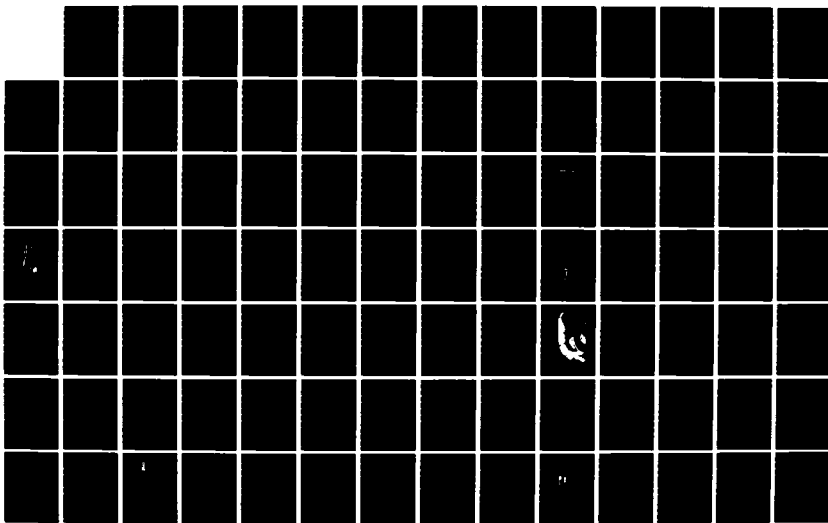
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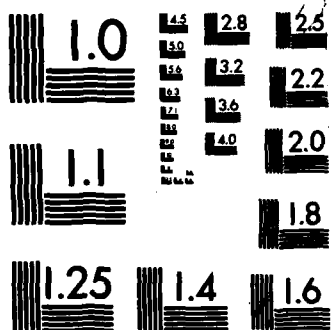
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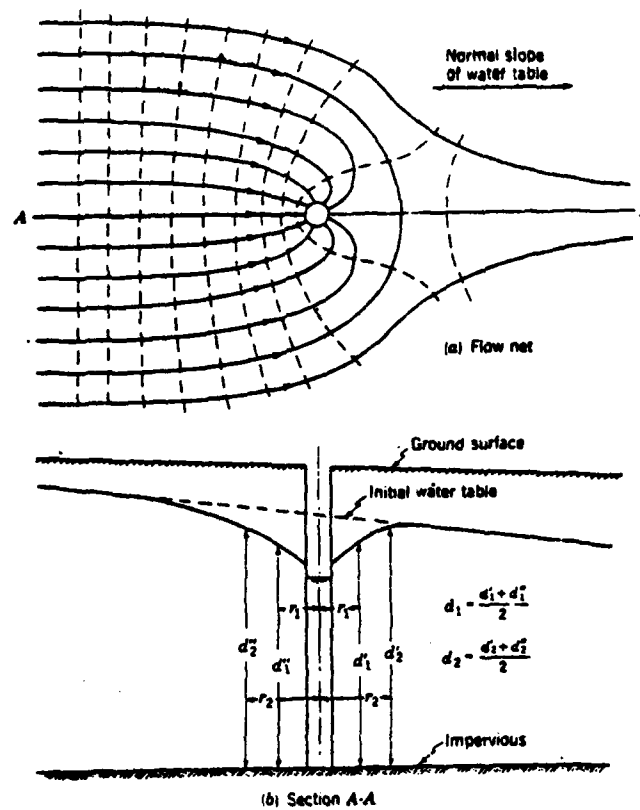


Figure 35. Flow to a Well in an Unconfined Aquifer with an Initially Sloping Water Table.

Source: Linsley, R.K. and J.B. Franzini, Water Resources Engineering, McGraw-Hill, Inc., New York, © 1972.

Frequently, more than one well may be operating in a particular area. If this is the case, pumping from one well may interfere with pumping from an adjacent well. The observed effect will be increased drawdown at points in the vicinity of the two wells. As shown in Figure 36 the drawdown at any point caused by the interference of several wells will be the sum of the drawdowns caused by each individual well. The increased drawdowns imply increased gradients and, consequently, increased velocities toward the wells.

Many confined aquifers are not perfectly bounded above or below. There may be several aquifers in a system, each pair separated by a confining bed (layer of less permeable material). For example, as shown schematically in Figure 37, an unconfined aquifer near ground surface may be underlain by a confining bed (e.g., clay layer or glacial till), which may in turn overlay a confined aquifer. Under natural conditions, a head difference will frequently exist between the upper and lower aquifers, such that flow occurs through the aquitard between the two aquifers. A situation such as this is termed a leaky aquifer system. The significance of pumping in such a system is in its potential for changing hydraulic gradients between the two connected aquifers. Depending on the original direction of flow and the location of the pumping well may increase flow in the original direction, decrease the flow or possibly reverse the direction of flow. As an example, consider the two-aquifer system mentioned above, and assume a higher potential in the confined aquifer than in the overlying unconfined aquifer, with a source of contamination existing in the unconfined aquifer. Development of wells in the confined aquifer will cause drawdown in potential. If the potential is reduced to values below those of the unconfined aquifer, flow will be induced into the confined aquifer, with the possible consequence of migration of contaminants between the two aquifers and degradation of water quality in the lower aquifer.

The preceding discussions of pumping effects all assume idealized representations of actual aquifer configurations. To quote Freeze and Cherry (1979):

In the real world, aquifers are heterogeneous and anisotropic; they usually vary in thickness; and they certainly do not extend to infinity. Where they are bounded, it is not by straight-line boundaries that provide perfect confinement. In the real world, aquifers are created by complex geologic processes that lead to irregular stratigraphy, interfingering of strata, and pinchouts and trendouts of both aquifers and aquitards.

As a result these discussions should be taken as indicative of the principles involved in understanding the effects of pumping on flow regimes rates, and the potential consequences with respect to pollutant migration. Application of these principles requires a detailed

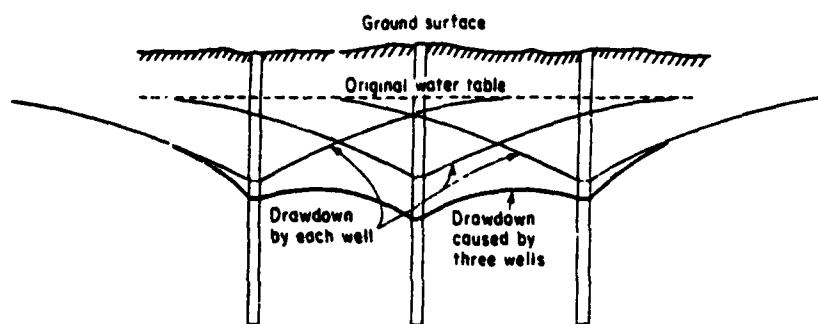


Figure 36. Effect of Interference Between Wells.

Source: Linsley, R.K., Jr., et al., Hydrology for Engineers, McGraw-Hill, Inc., New York, © 1975.

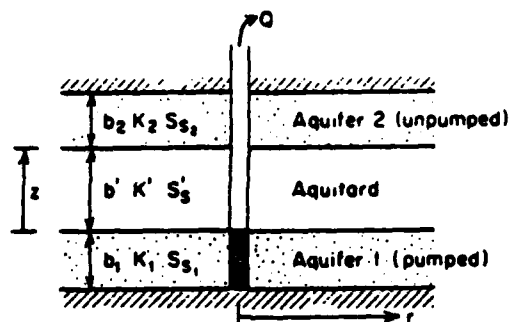


Figure 37. Schematic Diagram of a Two-Aquifer Leaky System.

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., © 1979.

understanding of the particular geology, stratigraphy, and flow regime of a particular region or site.

5. EFFECT OF SOLUBILITY AND DENSITY OF ORGANIC CONTAMINANTS

The rate and direction of movement of contaminants which have entered a groundwater system are functions of the local geology, groundwater flow regime, and the chemical and physical properties of the contaminant. This section qualitatively introduces the effect that variations in the solubility and the density of organic contaminants have on contaminant plume migration (the quantitative approach will be discussed in a later section). The first classification of contaminant is by solubility. Soluble contaminants dissolve into the groundwater and their subsequent movement is governed by Darcy's law, combined with hydrodynamic dispersion. Solids with low solubility are less likely to be transported in the groundwater. The movement of fluids that do not mix with water (immiscible fluids, such as oil) can be predicted using a more complex form of the general flow law that includes a term to describe the interactions between the different fluids and between each fluid and the solids matrix.

a. Soluble Contaminants

In saturated flow through a porous medium a portion of the flow domain is assumed to contain a certain mass of solute known as a tracer. As flow takes place, the tracer gradually spreads out and occupies more of the flow domain, beyond the region predicted by the average water flow alone. This spreading phenomenon is called hydrodynamic dispersion (also dispersion, immiscible displacement) in a porous medium (Bear, 1979). Figure 38 illustrates the difference between concentration levels with dispersion and without dispersion.

The actual mixing of the tracer with the uncontaminated water is caused by two microscopic processes: mechanical dispersion and molecular diffusion. Mechanical dispersion is the result of tracer velocity variation in direction and magnitude within a single pore space and between pore spaces of different sizes (Figure 39). This causes the individual stream lines to fluctuate with respect to the average flow (Figure 39). These phenomena cause the spreading of initially close groups of tracer particles until they occupy a larger and larger portion of the flow domain. Simultaneously, molecular diffusion produces an additional flux of tracer particles from regions of higher concentration to those of lower concentrations. This causes continual equalizing of tracer concentrations, first within a single streamline and then between two streamlines (Figure 39).

An "ideal tracer" is a solute that is inert with respect to its liquid and solid surroundings and does not affect the liquid's properties (Bear, 1972). Movement of this kind of solute can be predicted using the overall Darcy flow with a component for dispersion. However, solutes with large density contrasts with respect to water have a larger vertical component of dispersion. Figure 40 illustrates how a

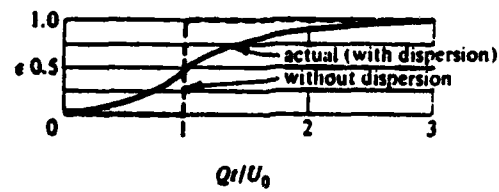


Figure 38. Transition Curve with Dispersion Versus Abrupt Change with No Dispersion

Source: Bear, J., Hydraulics of Groundwater, McGraw-Hill Book Company, New York, © 1979.

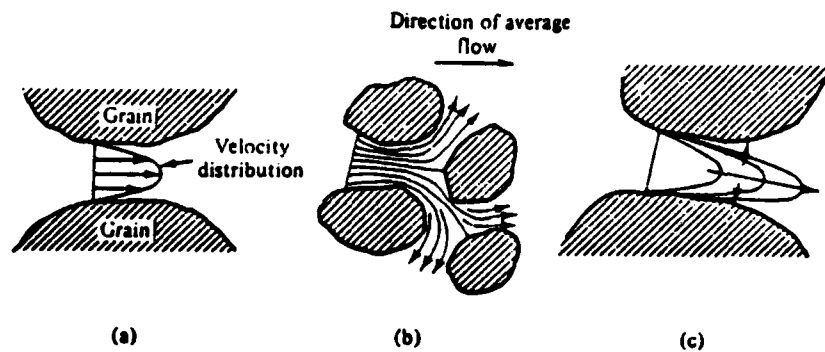


Figure 39. Hydrodynamic Dispersion Caused by Mechanical Dispersion (a,b) and Molecular Diffusion (c)

Source: Bear, 1979.

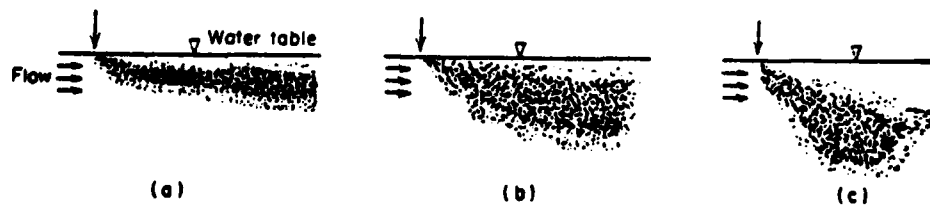


Figure 40. Effect of Density on Migration of Contaminant Solution in Uniform Flow Field, (a) Slightly More Dense than Groundwater; (b) and (c) Larger Density Contrasts

Source: Freeze, R.A. and J.A. Cherry, Groundwater, Prentice-Hall, Inc., 1979.

larger density contrast increases the importance of the dispersion component in accurately predicting tracer migration (Freeze and Cherry, 1979). The equations used to model solute transport by dispersion will be discussed in a later section.

b. Immiscible Flow

Fluids that do not readily mix with water (immiscible fluids, such as oil or nonaqueous phase liquid waste) do not flow according to the laws of hydrodynamic dispersion. The presence of these fluids causes water to adhere to the surface of the grains of the porous medium, a force known as surface tension. The immiscible fluid then flows through larger pore spaces, rarely displacing water from the smaller spaces. Capillary pressure is defined as the difference in pressure across the interface between the immiscible fluid and water (Davis and DeWiest, 1966). Capillary pressure only exists when two immiscible fluids are present, thus causing surface tension. The magnitude of capillary pressure strongly depends on the grain size of the porous material and on wetting properties of the fluids. This pressure term is an additional factor in the overall flow system. The existence of capillary pressure in a two-phase flow system means that the migration of an immiscible fluid is not solely dependent on the flow of groundwater. In fact, an immiscible fluid can migrate in a direction in complete opposition to the dominant flow system.

An example of contamination at the site of an oil spill is shown in Figure 41. The oil flows through the unsaturated zone, leaving residual oil absorbed by the soil particles until it intersects the water table. Once at the water table, oil floats on the surface of the water and is moved along the general flow of water. However, the oil will tend to be absorbed by soil particles until the volume of oil being transported is minimal (API, 1972). The added force of the capillary pressure can allow some of the insoluble oil to move upstream of the dominant flow (shown by the oil to the left of the original spill in Figure 41). Some of the components of oil are soluble and enter the groundwater itself (shown above the dotted line on Figure 41). These soluble components move by hydrodynamic dispersion causing a larger volume of groundwater to be contaminated downstream of the spill (Williams and Wilder, 1972). In the case of petroleum products, the more dense products (crude oil) have fewer soluble components than the less dense products (gas). One of the biggest problems with spills of light hydrocarbons is that the relative solubility increases the volume of groundwater that is contaminated (Matis, 1972).

An immiscible fluid that is more dense than water will also move according to the combined effects of the density difference, and the fluid-fluid and fluid-solid interfacial pressures. Because of the density contrast, the fluid will, in general, sink within the groundwater. A thorough understanding of the basic flow system is still required to predict the migration, and knowing all of the interactions between the fluids and the fluids and solids is fundamental to the prediction of fluid flow.

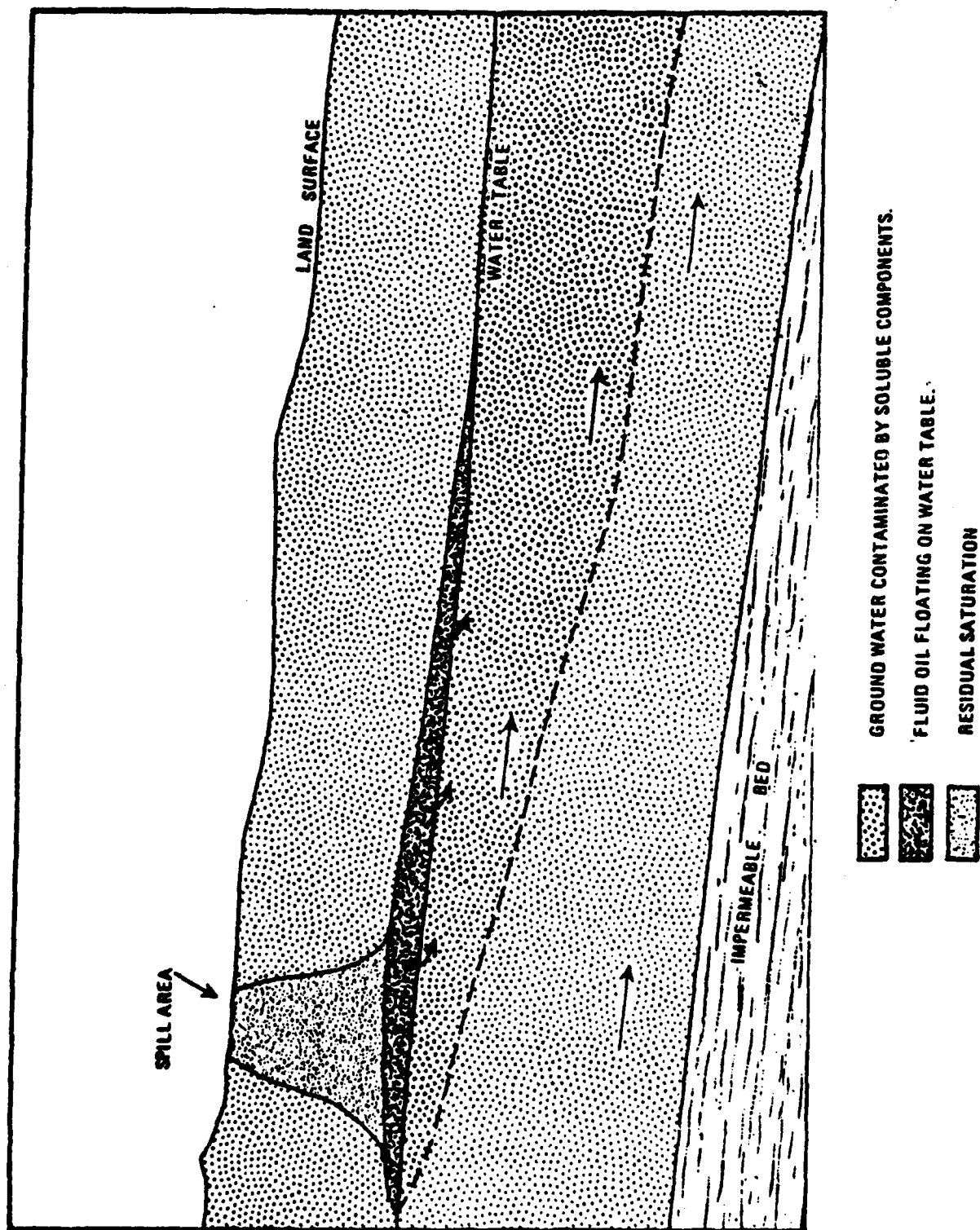


Figure 41. Groundwater Contaminated by an Oil Spill
 Source: American Petroleum Institute, *The Migration of Petroleum Products in Soil and Ground Water -- Principles and Countermeasures*, Publication No. 4149, © 1972.

A major problem in utilizing field measurements in two-phase flow cases is caused by a residual saturation of the immiscible liquid on soil particles that it has flowed past. Figure 41 shows a residual saturation in the zone above the water table. Fluctuation in the water table can increase the zone of residual saturation (Figure 42). A prolonged dry spell can cause a lowering of the water table that the petroleum will follow, thus deepening the zone of residual saturation. When the water table rises, at least a portion of the residual oil will be displaced by the water and will move vertically with the groundwater (API, 1972). Field measurements under such conditions must be carefully analyzed to discern the continuity of the phase as well as the concentration levels.

Immiscible fluids will tend to travel at velocities lower than the associated groundwater and will persist longer in a given area. Soluble contaminants (and soluble components of immiscible fluids) will tend to contaminate a larger volume of groundwater and at a rate faster than the dominant water flow.

6. FATE OF ORGANIC GROUNDWATER POLLUTANTS

a. Overview

In assessing the probable transport and fate of organic groundwater pollutants, the key processes to be considered may be listed in three groups:

(1) Equilibrium Partitioning of the Chemical:

- soil \leftrightarrow soil water (adsorption of solutes)
- water \leftrightarrow soil air (volatilization from solution)
- soil \leftrightarrow soil air (adsorption of vapors)

(2) Degradation of the Chemical:

- biodegradation
- hydrolysis (or elimination)
- oxidation or reduction (low importance)

(3) Transport of the Chemical:

- leaching (through unsaturated zone)
- transport with (and dilution in) groundwater
- volatilization and transport to the atmosphere
- erosion or entrainment of surface soils

These processes are considered in conjunction with the major phases of the soil/groundwater system: soil, soil water and (in the unsaturated zone) soil air. Figure 43 provides a schematic diagram of the system and processes.

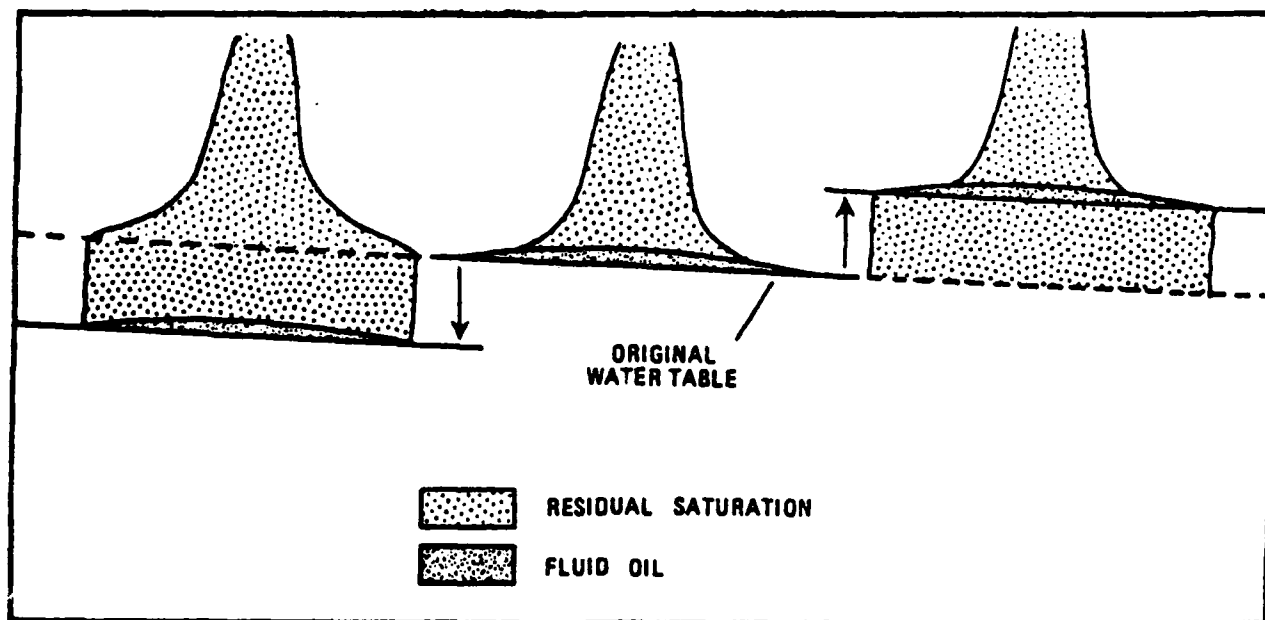
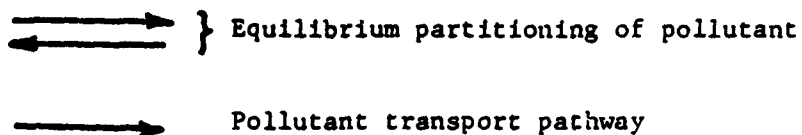
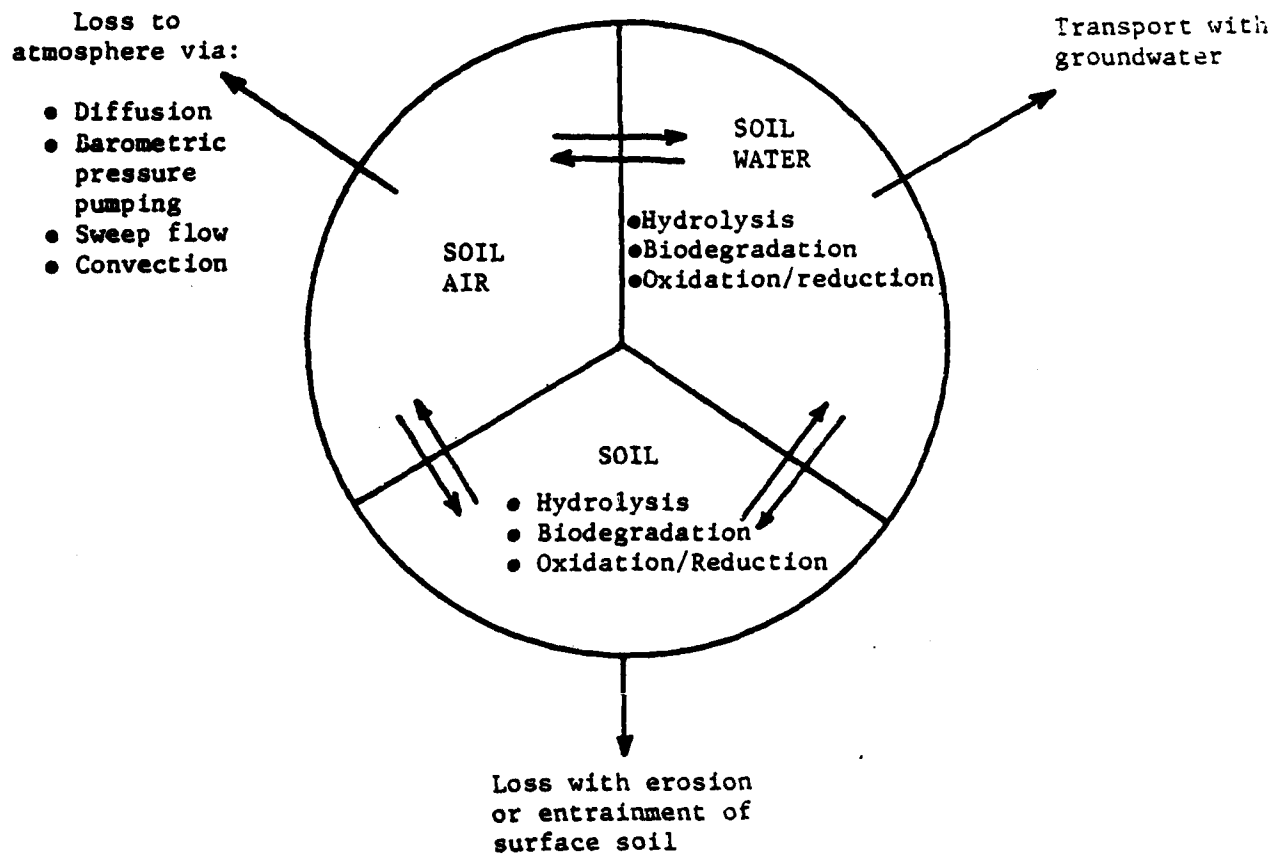


Figure 42. Contaminating Effect on Soil Caused by Vertical Movement of Oil on Fluctuating Water Table

Source: American Petroleum Institute, The Migration of Petroleum Products in Soil and Ground Water -- Principles and Countermeasures, Publication No. 4149, © 1972.



Source: Arthur D. Little, Inc.

Figure 43. Schematic Representation of Processes Affecting Organic Pollutants in the Soil/Groundwater System

The list of processes given above (and the following discussion in this section) presumes that no second (or immiscible) phase of organic material is present. A discussion of important processes associated with the fate of second-phase organics in the soil/groundwater system is provided in Section V.

An assessment of the relative importance of each of these transport and fate processes can be a difficult task because of the numerous chemical-specific and environment-specific properties affecting them (see Section V), and the likelihood that many of these properties will not be known.

An example of the variable behavior that may be seen for different groundwater pollutants is shown in Figure 44. The curves shown in this figure represent different concentration-time profiles that might be seen in an aquifer observation well following the continuous introduction of pollutants into the aquifer feeding the well. Some highly mobile and conservative (i.e., nondegradable) species, e.g., the chloride ion (Cl^-), will be affected principally by dispersion, and their observation-well concentrations will rise rapidly. Chemicals subject primarily to dispersion and adsorption, but not degradation, will also eventually reach high concentrations in the observation wells. Chemicals subject to degradation (e.g., hydrolysis or biodegradation), as well as adsorption and dispersion, will show a slower rise in concentration, may show a maximum, and will level off at some concentration (C) less than the injection concentration (C_0).

b. Equilibrium Partitioning

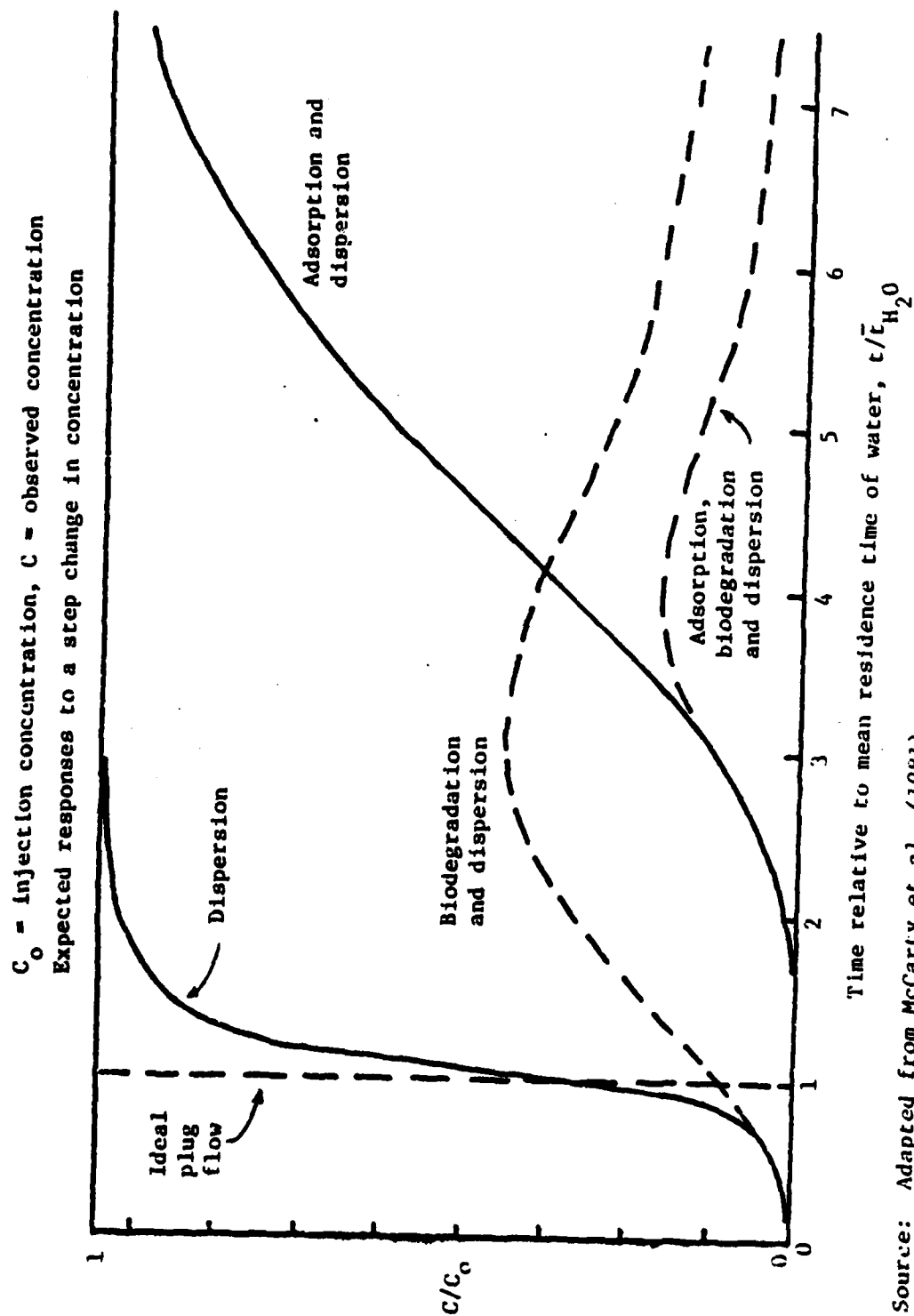
For phases in close physical contact, it will usually be reasonable to assume that the concentration of pollutants in the different phases is an equilibrium distribution, i.e., the distribution that would result - after a reasonable time period - when the rate of transfer from phase A \rightarrow B is the same as from B \rightarrow A. The assumption of equilibrium may be poor in some cases such as for: (1) rapid movement of groundwater through fissures and porous soils; (2) cold weather, especially when the ground is frozen; and (3) chemicals with very low solubility ($< 10 \mu\text{g/L}$) or high soil adsorption coefficient ($K_{oc} > 10^5$).

(1) Soil \leftrightarrow Soil Water *

Adsorption of organic solutes by soils will generally involve one or more of the following:

- (a) Adsorption on (or absorption in) the organic fraction of the soil;
- (b) Adsorption onto the surface of the inorganic soil minerals (especially clays); and

* Much of the information in this section is from Lyman (1982).



Source: Adapted from McCarty et al. (1981)

Figure 44. Effects of Dispersion, Adsorption, and Biodegradation on the Time Change in Concentration of an Organic Compound at an Aquifer Observation Well

- (c) For chemicals which act as bases (i.e., tend to lose a hydrogen ion, H^+), complexation, cation exchange, or other forms of interaction with electron-negative sites in the soil minerals.

Processes (a) and (b) are most important for neutral organic chemicals (e.g., hydrocarbon fuels, chlorinated solvents), and the relative importance of these two depends primarily on the organic carbon content of the soil. (The nature of the chemical and the surface area of the soil particles are also important factors.) The organic carbon content of soils may range from a high of about 40 percent [by weight] (peat, forest top soils) to 0.1 percent or less (sand, clay). Agricultural soils will usually have from 1 - 10 percent organic carbon. In all soils, the organic carbon content can be expected to decrease with soil depth, and may reach negligible amounts (< 0.1 percent) below one or two meters depth. In these deeper regions, the relative importance of adsorption processes (a) and (b) may be very uncertain and can only be resolved by laboratory experiments with the chemicals and soils in question.

The extent of adsorption is frequently described with the Freundlich equation:

$$x/m = KC^{1/n} \quad (2)$$

where x = amount adsorbed on soil (μg)

m = mass of soil (g)

K = adsorption coefficient

C = concentration in water ($\mu g/mL$)

n = parameter, usually in range of 0.7 to 1.1

Table 9 provides, for example, the Freundlich constants K and $1/n$ for Trichloroethylene (TCE) on a variety of soils; for comparison, the values for activated carbon adsorption of TCE are also shown. The last column in the table shows the amount that would be adsorbed on the soil (μg per g of soil) if the equilibrium concentration in the groundwater (C) was $100 \mu g/L$.

For soils with appreciable amounts of organic matter (> 0.1 percent for some chemicals, > 1 percent for others), it has been found that the amount of a chemical that is adsorbed - and, thus, the adsorption coefficient, K - is directly proportional to the organic carbon content of the soil. To represent this, a new adsorption coefficient, K_{oc} , is defined as K/f_{oc} where f_{oc} is the weight fraction of organic carbon in the soil ($0 < f_{oc} < 1$).

TABLE 9. SOIL ADSORPTION PARAMETERS FOR TRICHLOROETHYLENE

<u>Material</u>	<u>K</u>	<u>1/n</u>	<u>x/m (μg at $C = 100 \mu\text{g/L}$)</u>
Iron oxyhydroxide (goethite)	-	-	< 0.1
Amorphous manganese oxyhydroxide	0.0085	0.938	0.639
Kaolinite (a two-layer clay)	-	-	< 0.2
Montmorillonite (a three-layer clay)	0.0970	0.705	2.49
Soil from Wurtsmith AFB, Mich.	0.0759	0.324	0.337
Peat	0.148	0.737	4.41
Activated Carbon	377.0	0.623	6640.0

Source: Richter, 1981.

Numerous studies have shown that values of K_{oc} for a chemical are relatively constant (over a wide range of low concentrations) and reasonably independent of the soil used. Values of K_{oc} for organic chemicals range over 7 orders of magnitude (1 to 10,000,000) and, thus, extreme differences may be seen in the degree of adsorption for different chemicals. Table 9 provides K_{oc} values for a range of compounds. Reasonable estimates of K_{oc} may be obtained from regression equations which relate K_{oc} to other properties such as octanol-water partition coefficient, water solubility, bioconcentration factor in fish, and parachor (Lyman, 1982).

A final example will demonstrate the high variability that may be seen in soil adsorption of different organics. Table 10 provides information for benzene, trichloroethylene (TCE), and DDT, with assumed equilibrium concentrations in groundwater of 100 $\mu\text{g/L}$, 50 $\mu\text{g/L}$, and 1 $\mu\text{g/L}$, respectively. In these calculations, it is assumed that all adsorption is on (in) the organic carbon fraction of the soil, that $f_{oc} = 0.001$ (= 0.1 weight percent), that the soil has a bulk density of 2.05 g/cm^3 and a void volume of 50 percent, and that the Freundlich parameter $1/n$ has a value of 0.9. Values of K_{oc} are from Lyman (1982). The final column of Table 10 indicates that about 1/4 of the benzene and 1/2 of the trichloroethylene present in the soil/groundwater system are associated with the soil; the rest is in solution. For DDT, however, only 0.08 percent (1/1210) is in solution, while 99.92 percent is adsorbed on the soil.

The sample calculations above are representative of the type of analysis that may be carried out to assess the degree of adsorption for organics. Numerical predictions of this sort, however, should probably be considered to have an uncertainty of at least a factor of two (even when experimental chemical-specific and soil-specific data are used) when they are being applied to a specific site. This is due to a number of variables (see Section V) and the general inability to take all into account.

The effect of adsorption on the mobility of organic chemicals in groundwater is discussed later on in this section.

(2). Water -- Soil Air*

Partitioning of organic chemicals between groundwater and soil air (which may account for up to 50 percent of the volume of unsaturated zone soils) is important, not so much because of the mass distribution, but because transport of vapors may be significant. The important groundwaters here are clearly limited to the soil water in the unsaturated zone and the top layer of the groundwater in the saturated zone.

* Background information obtained from Thomas (1982a, 1982b).

TABLE 10. EXAMPLE ADSORPTION CALCULATIONS FOR BENZENE, TRICHLOROETHYLENE, AND DDT*

<u>Chemical</u>	<u>Water Concentration (µg/L)</u>	<u>K_{oc}</u>	<u>K</u>	<u>Amount Adsorbed</u>		<u>Amount in Soil/Amount in Water</u>
				<u>µg/g</u>	<u>µg/cm³</u>	
Benzene	100	83	0.083	0.0104	0.026	0.26
TCE	50	160	0.16	0.0108	0.027	0.54
DDT	1	243,000	243.0	0.485	1.21	1210.0

* See text for conditions of calculations.

Source: Arthur D. Little, Inc.

At low solute concentrations, the concentration of the chemical in the vapor phase will be directly proportional to its concentration in water:

$$C_{\text{air}} = H \cdot C_{\text{water}} \quad (3)$$

The constant of proportionality, H , is called Henry's law constant. H is temperature-dependent, and, like K_{oc} , may range over 7 orders of magnitude for different chemicals.

The units used for H are variable, depending upon user preference. If both C_{air} and C_{water} are expressed in similar units (e.g., g/m³), then a 'nondimensional' H is obtained. Such units are common in the older literature. More recently, H is reported with units of atm · m³/mol or - most recently - in the SI units of kPa · m³/mol. Table 11 lists values of H for several chemicals. A critical review of values of H for several organic chemicals was recently prepared by Mackay et al. (1982).

For chemicals of limited solubility (< 0.1 mole fraction), Henry's law constant may be estimated from the ratio of the chemicals vapor pressure (P_{vp}) to water solubility (S):

$$H = P_{vp} / S \quad (4)$$

Since, for most chemicals, P_{vp} is a much stronger function of temperature than S , values of H will increase with increasing temperature in rough proportion to the increase in P_{vp} .

An inspection of the values of H' (nondimensional H) in Table 11 shows that the mass distribution of a chemical between groundwater and soil air is weighted on the water side for all except the most volatile chemicals (e.g., ethyl bromide, vinyl chloride, etc.). Table 12 indicates, for example, how three chemicals would be partitioned between the soil water and soil air (in the unsaturated zone) if it were assumed the air and water were of equal volume and that soil adsorption was negligible.

(3) Soil -- Soil Air

Relatively few data are available which describe the nature and extent of organic vapor adsorption onto soils, and this process is frequently ignored in models simulating the transport of organic vapors through soil.

To a first approximation, the relative concentrations of a chemical in soil air and soil should be proportional to the chemical's vapor pressure and inversely proportional to the square root of solubility:

TABLE 11. VALUES OF HENRY'S LAW CONSTANT FOR SELECTED CHEMICALS

Chemical	Henry's Law Const.		Chemical	Henry's Law Const.	
	$\frac{H}{\left(\frac{\text{atm-cm}^3}{\text{mol}}\right)}$	H' (Mond-dim.)		$\frac{H}{\left(\frac{\text{atm-cm}^3}{\text{mol}}\right)}$	H' (Mond-dim.)
Low Volatility ($H < 3 \times 10^{-7}$)			High Volatility ($H > 10^{-3}$)		
3-Bromo-1-propanol	1.1×10^{-7}	4.6×10^{-6}	Ethylene dichloride	1.1×10^{-3}	4×10^{-2}
Dieldrin	2×10^{-7}	8.9×10^{-6}	Naphthalene	1.15×10^{-3}	4.9×10^{-2}
Middle Range ($3 \times 10^{-7} < H < 10^{-3}$)			Biphenyl	1.5×10^{-3}	6.8×10^{-2}
Lindane	4.9×10^{-7}	2.2×10^{-5}	Aroclor 1254	2.7×10^{-3}	1.2×10^{-1}
m-Bromonitrobenzene	1.6×10^{-6}	7.4×10^{-5}	Methylene chloride	3×10^{-3}	1.3×10^{-1}
Pentachlorophenol	3.4×10^{-6}	1.5×10^{-4}	Aroclor 1248	3.5×10^{-3}	1.6×10^{-1}
4-t-Butylphenol	9.1×10^{-6}	3.8×10^{-4}	Chlorobenzene	3.7×10^{-3}	1.65×10^{-1}
Triethylamine	1.3×10^{-5}	5.4×10^{-4}	Chloroform	4.8×10^{-3}	2.0×10^{-1}
Aldrin	1.4×10^{-5}	6.1×10^{-4}	o-Xylene	5.1×10^{-3}	2.2×10^{-1}
Nitrobenzene	2.2×10^{-5}	9.3×10^{-4}	Benzene	5.5×10^{-3}	2.4×10^{-1}
Epichlorohydrin	3.2×10^{-5}	1.3×10^{-3}	Toluene	6.6×10^{-3}	2.8×10^{-1}
DDT	3.6×10^{-5}	1.7×10^{-3}	Aroclor 1260	7.1×10^{-3}	3.0×10^{-1}
Phenanthrene	3.9×10^{-5}	1.7×10^{-3}	Perchloroethylene	8.3×10^{-3}	3.4×10^{-1}
Acenaphthene	1.5×10^{-4}	6.2×10^{-3}	Ethyl benzene	8.7×10^{-3}	3.7×10^{-1}
Acetylene tetrabromide	2.1×10^{-4}	8.9×10^{-3}	Trichloroethylene	1×10^{-2}	4.2×10^{-1}
Aroclor 1242	5.6×10^{-4}	2.4×10^{-2}	Mercury	1.1×10^{-2}	4.8×10^{-1}
Ethylene dibromide	6.6×10^{-4}	2.9×10^{-2}	Methyl bromide	1.3×10^{-2}	5.6×10^{-1}
			Cumene (isopropyl benzene)	1.5×10^{-2}	6.2×10^{-1}
			1,1,1-Trichloroethane	1.8×10^{-2}	7.7×10^{-1}
			Carbon tetrachloride	2.3×10^{-2}	8.7×10^{-1}
			Methyl chloride	2.4×10^{-2}	3.6×10^{-1}
			Ethyl bromide	7.3×10^{-2}	3.1
			Vinyl chloride	2.4	89
			2,2,4-Trimethyl pentane	3.1	129
			n-Octane	3.2	136
			Fluoro-trichloromethane	5.0	
			Ethylene	> 8.6	~ 360

Source: Thomas, 1982b.

TABLE 12. EXAMPLE AIR-WATER PARTITIONING CALCULATIONS*

<u>Chemical</u>	<u>H' (non-dim.)</u>	<u>Amount in Water/Amount in Air</u>
Benzene	0.24	4.2
Trichloroethylene	0.42	2.4
DDT	0.0017	590.0

* See text for conditions of calculation.

Source: Arthur D. Little, Inc.; values of H' from Thomas (1982b).

$$\frac{C_{\text{air}}}{C_{\text{soil}}} \approx \frac{H}{K} = \frac{P_{\text{vp}}/S}{K} \approx k P_{\text{vp}}/S^k \quad (5)$$

where:

- H = Henry's law constant
- K = Freundlich soil adsorption coefficient
(1/n assumed = 1)
- P_{vp} = vapor pressure
- S = water solubility
- k = constant of proportionality

With P_{vp} in units of atm and S in units of mol/m³, k would appear to be on the order of 100; this would provide a dimensionless ratio for $C_{\text{air}}/C_{\text{soil}}$. Sample calculations using equation 3-4 ($k P_{\text{vp}}/S^k$ with $k = 100$) indicate that the $C_{\text{air}}/C_{\text{soil}}$ ratios for DDT, trichloroethylene and benzene are about 1×10^{-5} , 5, and 2, respectively.

c. Degradation

Only two processes, biodegradation and hydrolysis, appear to have the potential to effect any significant amount of degradation of organic chemicals in the soil/groundwater system. In many instances, the refractory nature of the chemicals and/or environmental variables (e.g., sterile soils, cold weather) may reduce even these processes to minimal importance.

The third type of reaction mentioned in the overview, oxidation/reduction, can only be important when potent oxidizing or reducing agents are present. Such agents do not exist in natural soil groundwater systems. In natural systems, near-surface soils (and soil waters) will contain oxygen, a very mild oxidizing agent; and in deeper soils such mild reducing agents as H₂ and CH₄ may be present in small amounts. Direct oxidation or reduction by such agents is unlikely to be significant except for the most reactive of compounds.

(1) Biodegradation*

Biodegradation is one of the most important environmental processes that cause the breakdown of organic compounds. This capability is put to use, for example, in biological wastewater treatment plants and in the disposal of some wastes on land ("land farming") in a manner that promotes biodegradation. Natural biodegradation of a wide variety of organic chemicals can take place in surface water and soil systems.

The most significant group of organisms involved in biodegradation are microorganisms, including mostly a large variety of bacteria, fungi, and protozoa. The ability of various microorganisms to degrade

* Background information for this section was obtained from Scow (1982).

certain chemicals varies widely, and the importance of environmental conditions (warm temperature; adequate food, water and nutrients; pH; etc.) cannot be overstated.

The quantity of such organisms available to degrade chemicals is also a key factor. Near-surface soils in fields and woods may contain 100-1000 or more kilograms (wet wt) per hectare of these living microorganisms representing up to 10 individual microorganisms per gram of soil (Scow, 1982). The population density of soil microorganisms, however, can drop off rapidly with increasing soil depth. This may be caused by a combination of factors, including decreasing amounts of food (organic matter) and nutrients with depth, lesser amounts of oxygen for anaerobic microorganisms, and a filtering of the organisms by the soil. Only under landfills, or in other areas where organic matter exists in deep soils, can biodegradation be expected to be a significant degradation process below 1 or 2 meters of the soil surface.

When a soil is heavily contaminated, e.g., by contamination from a leaking chemical lagoon, the combination of quantity and toxicity (to microorganisms) may effectively block biodegradation. In less severe cases, biodegradation may follow a period of acclimation lasting days or weeks.

Except for a few limited cases, rates of biodegradation in soil cannot be predicted for specific chemicals, and laboratory tests must be carried out. Similarly, the reaction pathways (through intermediate chemicals) leading sometimes to ultimate degradation must be determined in the laboratory.

Understandably, most of the existing data on rates of biodegradation in soils are for pesticides. Tables 13 and 14 provide an assortment of such data which may be illustrative only of rates for pesticides (often difficult to degrade) in near-surface soils. All of the rate constants in these tables are for primary degradation (i.e., any alteration of the initial compound) and imply a first order reaction, i.e.:

$$\frac{-dc}{dt} = kC \quad (6)$$

where c = chemical concentration
 t = time
 k = degradation rate constant

The use of Equation 6 is exemplified by assuming a soil with 1 mg/L of lindane. The value of $-dc/dt$ is thus $(1 \text{ mg/L}) \times (0.0026/\text{day}) = 0.0026 \text{ mg/L} \cdot \text{day}$. With first order reactions, the half-life (time for 50 percent to disappear) is $0.693/k$. For lindane, the half-life in soil (under the test conditions) would, thus, be 270 days.

TABLE 13. BIODEGRADATION RATE CONSTANTS FOR
ORGANIC COMPOUNDS IN SOIL^a (DAY⁻¹)

Compound	Test Method	
	Die-Away	¹⁴ CO ₂ Evolution
Aldrin, Dieldrin	0.013	
Atrazine	0.019	0.0001
Bromacil	0.0077	0.0024
Carbaryl	0.037	0.0063
Carbofuran	0.047	0.0013
Delapon	0.047	
DDT	0.00013	
Diazinon	0.023	0.022
Dicamba	0.022	0.0022
Diphenamid		0.123 ^b
Fonofos	0.012	
Glyphosate	0.1	0.0086
Heptachlor	0.011	
Lindane	0.0026	
Linuron	0.0086	
Malathion	1.4	
Methyl parathion	0.16	
Paraquat	0.0016	
Parathion	0.029	
Phorate	0.0084	
Picloram	0.0073	0.0008
Simazine	0.014	
TCA	0.059	
Terbacil	0.015	0.0045
Trifluralin	0.008	0.0013
2,4-D	0.066	0.051
2,4,5-T	0.035	0.029

a. All constants are from soil incubation studies. Except where noted, source is Rao and Davidson (1980), a compilation of first order rate constants derived from data published from other studies.

b. Optimum degradation rate, from Donigan et al. (1977). Test method not specified.

TABLE 13. BIODEGRADATION RATE CONSTANTS FOR ORGANIC COMPOUNDS
IN ANAEROBIC SYSTEM^a

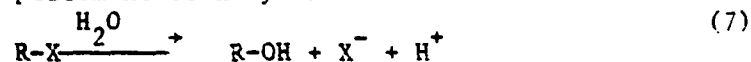
Compound	(DAY ⁻¹)		In Sewage Sludge ^b
	In Soil ^a		
	Die-Away	¹⁴ CO ₂ Evolution	
Carbofuran	0.026		
DDT	0.0035		
Endrin	0.03		
Lindane		0.0046	
PCP		0.07	
Trifluralin	0.025		
Mirex			0.0192
Methoxychlor			9.6
2,3,5,6-Tetrachlorobenzene			12.72
Bifenox			6.27

a. Flooded soil incubation studies as reported in Rao and Davidson (1980), a compilation of first order rate constants derived from data published from other sources.

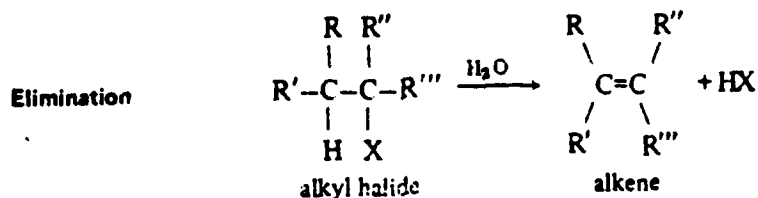
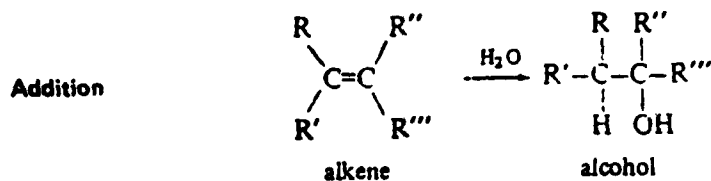
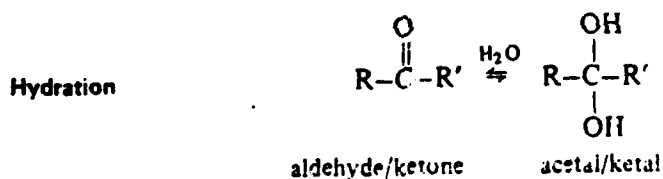
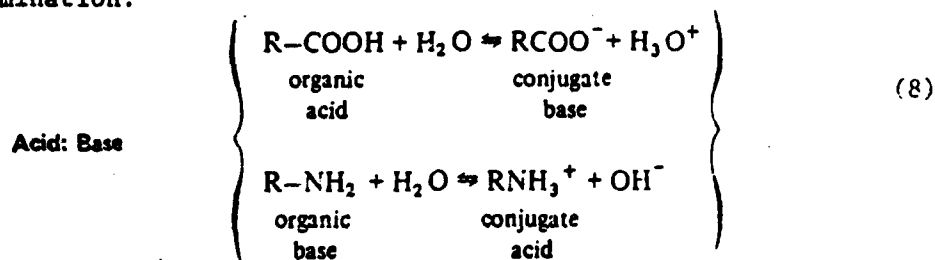
b. As reported by Geer (1978). Test method not specified.

(2) Hydrolysis*

Hydrolysis is a chemical transformation process in which an organic molecule, RX, reacts with water, cleaving a carbon-X bond and (generally) forming a new carbon oxygen bond. The net reaction is most commonly a direct replacement of X by OH:



Hydrolysis is not just one reaction type (as the example above), but a family of reactions involving attack by water at the sites of various functional groups (e.g., alkyl halides, esters, epoxides, nitriles, carbamates, and organophosphates). The reaction mechanism and products may differ significantly from compound to compound. Other types of reactions (of organic chemicals with water) that will also have to be considered in some cases include acid:base, hydration, addition, and elimination:



* Background information obtained from Harris (1982).

Except for such reactions as acid:base, which are fast and reversible, most of the hydrolysis reactions of interest will involve highly variable rate constants, reaction pathways, and reaction products. Figure 45 shows, for example, that half-lives for degradation via hydrolysis range over at least 7 orders of magnitude under typical ambient conditions (pH 7, 25°C).

Temperature, pH and the presence of catalysts are very important variables determining the rate of hydrolysis. For temperature, if the energy of activation for hydrolysis is assumed to be 17-18 kcal/mol (for most chemicals, it is in the range of 12-25 kcal/mol), the following rules of thumb may be used for temperatures in the 0 - 50°C range:

- A 1°C increase (decrease) in temperature causes a 10 percent increase (decrease) in the rate constant;
- A 10°C increase (decrease) will increase (decrease) the rate constant by a factor of 2.5;
- A 25°C increase (decrease) will increase (decrease) the rate constant by a factor of 10.

Many hydrolysis reactions are catalyzed by the presence of OH⁻ (bases), H⁺ (acids), or other constituents (e.g., certain heavy metals such as Cu⁺⁺), which may be present in the groundwater. Thus, tests with site-specific waters may be desirable in some cases. The extent of adsorption on soil is another factor which may affect the rate of hydrolysis. The available literature provides little guidance in this area.

It is generally observed that hydrolysis of organic chemicals in water is first order in the concentration of the organic species, [RX]; i.e.:

$$-d[RX]/dt = k_T [RX] \quad (9)$$

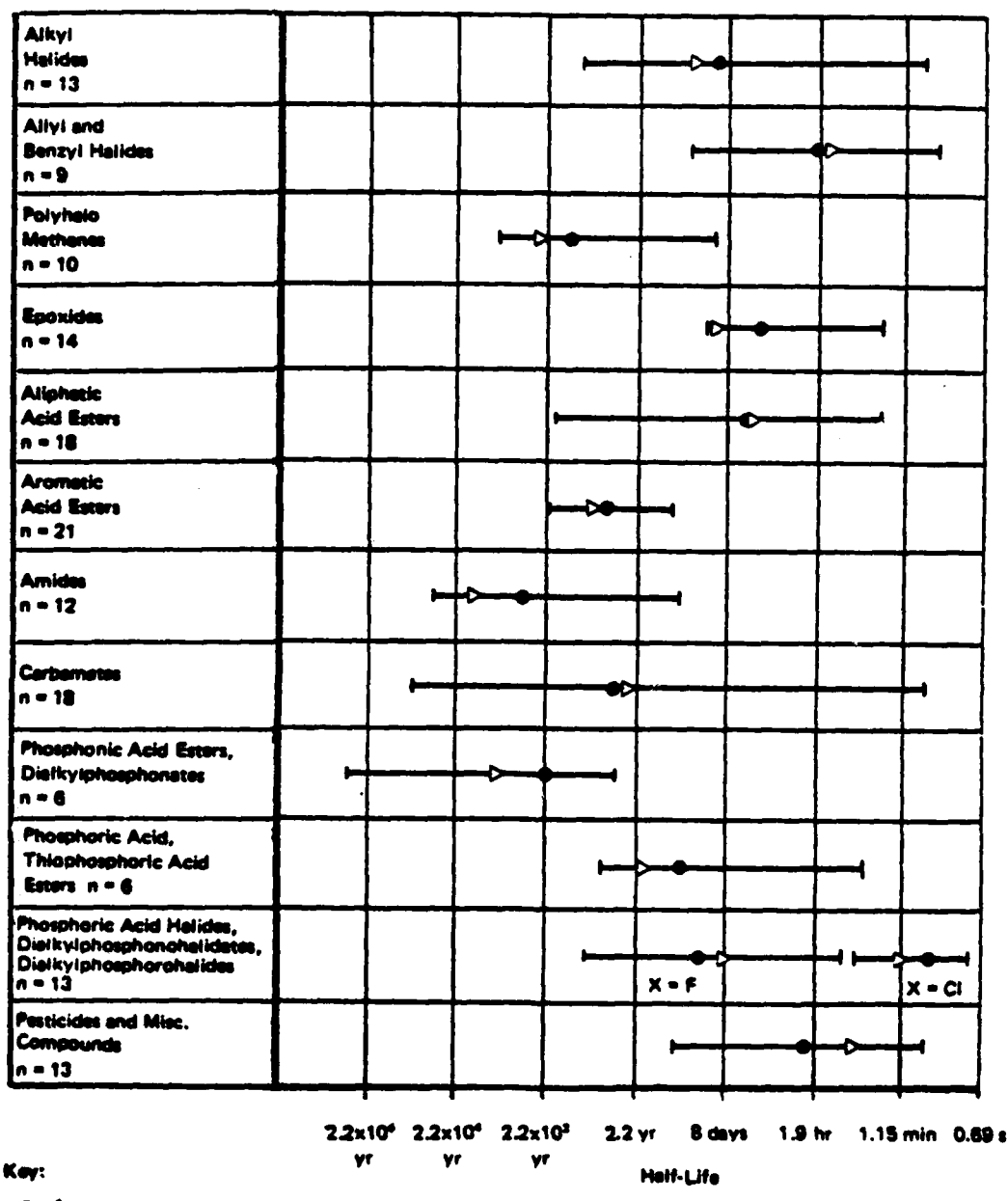
where:

- [RX] = chemical concentration
- t = time
- k_T = total hydrolysis rate constant

To take acid and base catalysis into consideration, k_T is usually considered to consist of three terms representing acid-catalyzed, neutral, and base-catalyzed reactions:

$$k_T = k_H[H^+] + k_O + k_{OH}[OH^-] \quad (10)$$

Many organic functional groups (Table 15) are relatively or completely inert with respect to hydrolysis. Other functional groups which may hydrolyze under environmental conditions are listed in Table 16.



Source: Adapted by Fiksel and Segal (1980) from data of Maybey and Mill (1978).

Figure 45. Examples of the Range of Hydrolysis Half-Lives For Various Types of Organic Compounds in Water at pH 7 and 25°C

TABLE 15. TYPES OF ORGANIC FUNCTIONAL GROUPS THAT ARE GENERALLY RESISTANT TO HYDROLYSIS^a

Alkanes	Aromatic nitro compounds
Alkenes	Aromatic amines
Alkynes	Alcohols
Benzenes/biphenyls	Phenols
Polycyclic aromatic hydrocarbons	Glycols
Heterocyclic polycyclic aromatic hydrocarbons	Ethers
Halogenated aromatics/PCBs	Aldehydes
Dieldrin/aldrin and related halogenated hydrocarbon pesticides	Ketones
	Carboxylic acids
	Sulfonic acids

a. Multifunctional organic compounds in these categories may, of course, be hydrolytically reactive if they contain a hydrolyzable functional group in addition to the alcohol, acid, etc., functionality.

Source: Harris (1982)

TABLE 16. TYPES OF ORGANIC FUNCTIONAL GROUPS THAT ARE POTENTIALLY SUSCEPTIBLE TO HYDROLYSIS

Alkyl halides	Nitriles
Amides	Phosphonic acid esters
Amines	Phosphoric acid esters
Carbamates	Sulfonic acid esters
Carboxylic acid esters	Sulfuric acid esters
Epoxides	

Source: Harris, 1982

In a few limited cases, it is possible to predict the rate of hydrolysis for organic compounds (Harris, 1982), but even here the uncertainties involved would suggest that estimated rate constants be considered order-of-magnitude estimates.

d. Transport

As was shown in Figure 43, the three transport processes that require consideration for organics in the soil/groundwater system are:

- transport with water - (deletes percolation through the unsaturated zone and movement with the groundwater);
- volatilization and transport of the vapors, through the unsaturated zone, to the atmosphere;
- erosion or entrainment of (contaminated) surface soils.

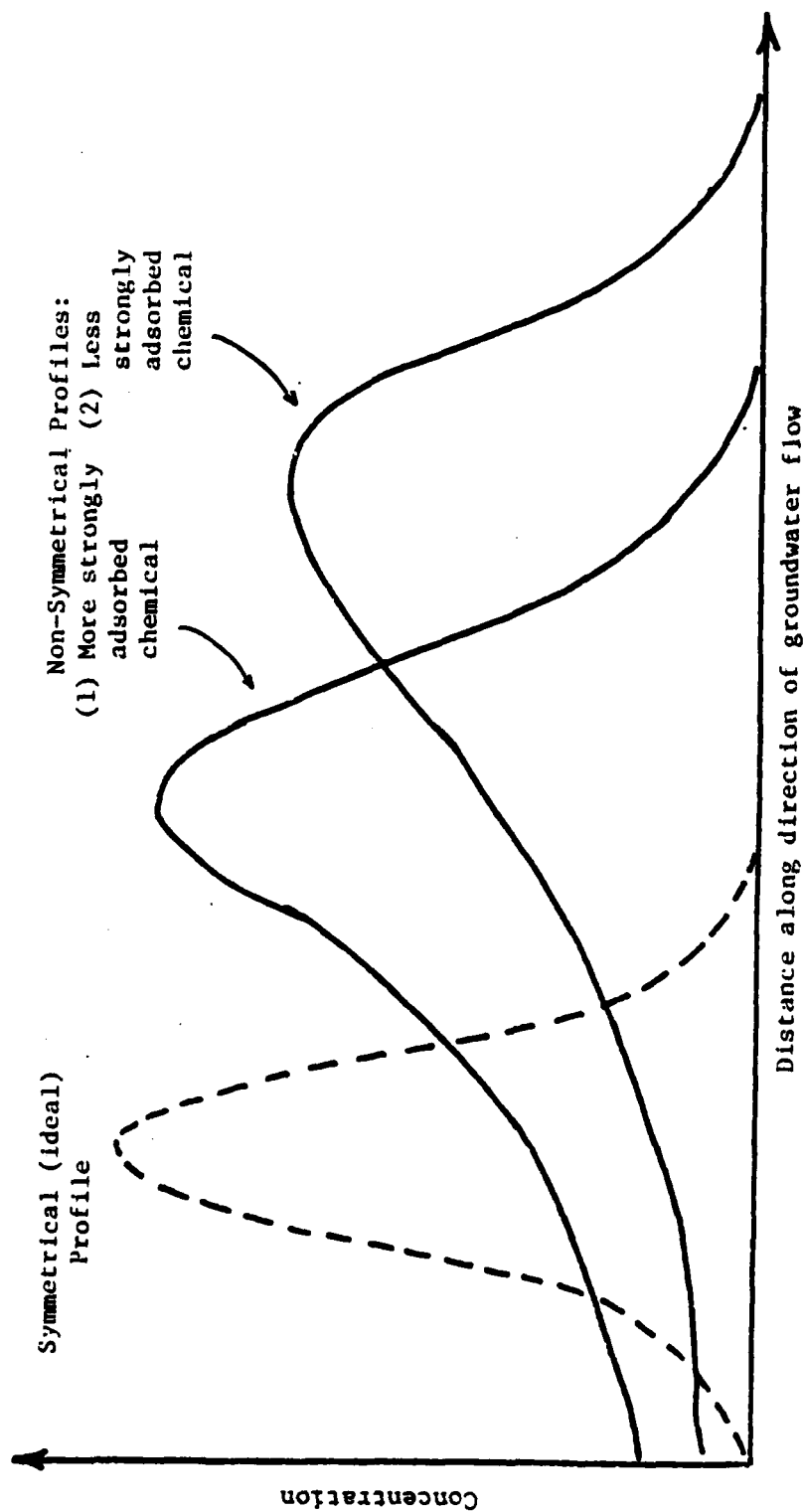
Only the first two processes are significant for pollutants already in groundwater, and some additional discussion on them is provided below.

(1) Transport With Water

Pollutants will be transported with groundwater, primarily in solution. The most important factor to understand is the chromatographic effect whereby chemicals with higher soil adsorption coefficients will be retarded with respect to those with lower soil adsorption coefficients.

A significant body of literature exists on leaching, including numerous soil column leaching tests, the measurement of retention factors (R_f), and the development of predictive mathematical models (See Hamaker, 1975; Tinsley, 1979; Letey and Farmer, 1974; Thibodeaux, 1979; Fried and Combarous, 1971; Leistra, 1973; Letey and Oddson, 1972; and Section V of this report).

If simple equilibrium adsorption, molecular diffusion, and mixing were the only processes involved, then - in homogeneous soils - the concentration-depth (or distance) profile of a pollutant in response to a pulse of injected pollutant would include a symmetrical peak; this is shown by the dashed curve in Figure 46. In fact, nonsymmetrical peaks (involving a longer tail and sharper front) are often seen, especially at higher water flow rates. Figure 46 shows schematically the nature of such curves. The nonsymmetrical profiles may be due to nonequilibrium adsorption kinetics (i.e., rate of desorption < rate of adsorption), and/or to changes in the effective adsorption coefficient due to the presence of previously adsorbed chemical.



Source: Arthur D. Little, Inc.

Figure 46. Schematic Representation of Concentration-Distance Profiles for Pollutants Moving through Soil (All Profiles Assume a Discrete, One-Time Injection of the Pollutant)

(2) Volatilization and Vapor Transport

Four processes appear to be involved in chemical volatilization (from groundwaters) and the subsequent loss of vapors to the atmosphere:

(a) Diffusion

- Driven by concentration gradient, in soil-air, of chemical between groundwater and soil surface.
- Surface winds deplete surface concentrations.

(b) Sweep Flow

- Bulk transport of the pollutant vapors along with gases (e.g., methane, carbon dioxide) generated in the soil.
- Very important for landfills.

(c) Barometric Pressure Pumping

- Continual compression and expansion of soil air follows changes in barometric pressure.
- The short term volatilization flux of pollutants is significantly affected.
- Most important where depth to contaminated groundwater or waste is small compared to depth of unsaturated zone.

(d) Thermal Gradients

- Diurnal, short term and seasonal air temperature changes will lead to thermal gradients in the top few meters of the soils.
- In winter, the presence of cold (more dense) air at soil surface and warmer (less dense) air below could lead to convection currents.

Many factors are involved in these processes (Table 17). Models for the prediction of volatilization rates frequently ignore all processes except diffusion. The current knowledge on this volatilization process is rather limited, although a number of experimental (laboratory and field) and theoretical studies have been conducted (See Thomas, 1982a; Thibodeaux, 1979, 1981; Shen, 1981; and Farmer et al., 1980).

TABLE 17 FACTORS AFFECTING RATE OF VOLATILIZATION FROM SOIL

METEOROLOGICAL

- Changes in barometric pressure
- Air (and soil) temperature
- Rainfall, infiltration
- Snow cover
- Ground frost
- Wind speed
- Relative humidity

SITE AND SOIL

- Type and extent of soil coverage
- Soil porosity
- Moisture content of soil
- Lateral extent (reach) of site
- Protection from wind
- Adsorption capacity of soil (organic carbon content)

WASTE

- Form of waste (pure chemical, mixture, aqueous solution)
- Area covered by waste
- Physicochemical properties (D_s , H , γ , K_{OC} , P_{VP} , S , . . .) relating to volatilization, dissolution, adsorption, diffusion, partitioning, etc.
- Stability (resistance to hydrolysis, etc.)

Source: Arthur D. Little, Inc.

What is clear, however, is that the volatilization loss pathway can be significant, not only for chemicals with high concentrations in soil air, but also those (e.g., DDT, polychlorinated biphenyls, polynuclear aromatics) which have very high soil adsorption coefficients and are resistant to degradation. For this latter group of chemicals, downward migration through soils is almost negligible, and slow volatilization is the only transport pathway open.

SECTION IV

FIELD AND LABORATORY TECHNIQUES FOR ASSESSING GROUNDWATER CONTAMINATION

1. DRILLING METHODS

As part of the subsurface investigation of a site, wells may have to be bored or drilled in order to sample the sediment and rock, and/or to monitor groundwater flow. The method (of boring or drilling) employed to sink a well depends on the depth required, the use of the well, and on the material (sediment or rock) present at the site.

Most unconsolidated sediment (except sand and gravel) can easily be penetrated by auger boring, but only to limited depths. For drilling into rock, cable-tool percussion equipment works the best while rotary drilling is well suited for deep holes in unconsolidated sediments (especially sand and gravel). A brief description of each of these drilling methods follows, along with a summary of the advantages and disadvantages of each method.

a. Auger Boring

Figures 47 and 48 show examples of several augers. These tools are used to bore holes according to the procedure described in EPA (1980b):

"In auger boring, the hole is advanced by rotating and pressing a soil auger into the soil and withdrawing and emptying the auger when it is full. Since water tends to prevent accumulation of soil in the auger, the borehole is kept dry as much as possible. Hand augering can be easy or difficult depending upon whether clay, sand, or gravel, respectively, is being removed. Small-diameter helical or posthole augers can be used to advance 5 to 30 cm (12-inch) diameter holes by hand to depths of 6 to 9 meters (20 to 30 feet) (Figure 47). If a tripod and pulley are set up to aid in pulling the auger from the hole, depths of 24 meters (80 feet) can be reached. If the hole can be kept open below the water table (usually only in cohesive material), screen and casing can be set, backfilled, and developed.

The process becomes much simpler and less time consuming if power augers are used. Here, flights of spiral, hollow-stem augers are forced into the ground while being

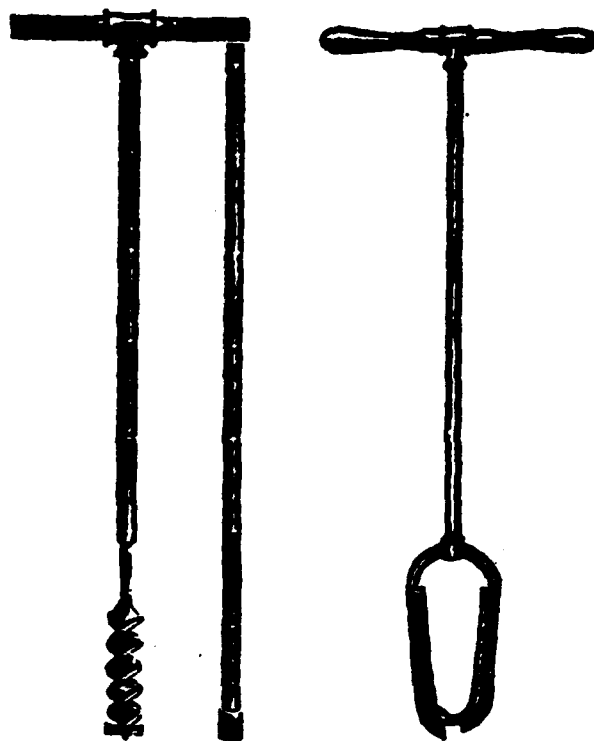


Figure . 47. Small Helical Augers (left) and a posthole or Iwan Auger (right).

Source: EPA, 1980b.

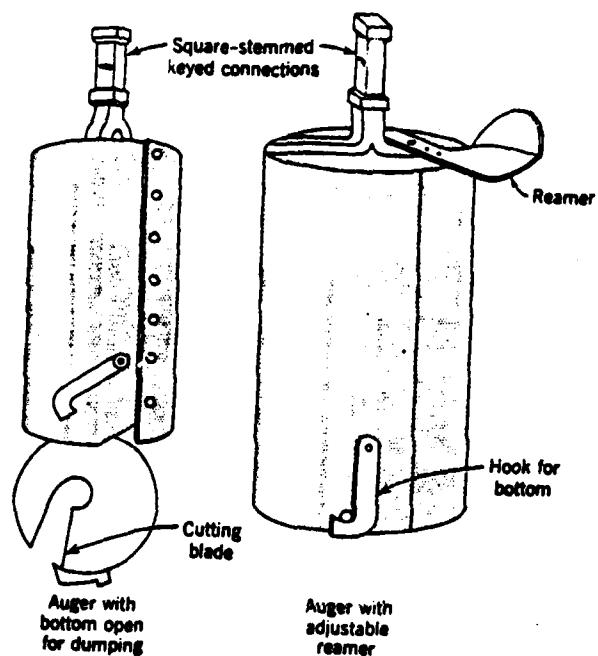


Figure 48. Augers Used for Boring Wells.

Source: Todd, D.K., Groundwater Hydrology, John Wiley and Sons, Inc., New York, © 1959.

rotated; the spiral action of the augers conducts cuttings to the surface (Figure 47). On completion of drilling, a small-diameter casing and well point are pushed to the desired depth. When bucket augers are used, a large diameter barrel (up to 122 cm (48 inches)) fitted with cutting blades is rotated into the ground until it is full (Figure 48). The earth-laden bucket is then brought to the surface, pulled to one side, and dumped. This process is repeated to completion depth."

The procedure for securing a collapsing bored hole (or drilled hole) is through the use of metal, concrete or tile casings. Casings are cylindrical tubes inserted to physically hold up the sides of the hole for continued boring through the casing. Augers work best in formations that do not collapse and are as effective as any other penetrating device where cohesive clay formations are encountered (Todd, 1959).

The following list is a cumulative summary of the advantages and disadvantages of auger boring equipment from EPA (1980b), Sowers (1970) and Todd (1959).

Auger Boring

Advantages

Inexpensive.

Small, high-mobility rigs can reach most sites.

Can be used to quickly construct shallow well clusters.

If borehole prematurely reaches refusal depth, setup time is low and rig can be moved rapidly.

No drilling fluids introduced into the borehole; no possibility of diluting formation water.

Disadvantages

Limited penetration; normally 30 to 46 meters (100 - 150 feet) maximum (6 meters for hand augers).

Vertical leakage through sediment left in borehole through which drive point is forced to completion depth. No method to isolate screened zones of aquifer.

Careful attention during drilling is required to obtain correct log of formation materials penetrated.

Unable to collect groundwater samples during drilling.

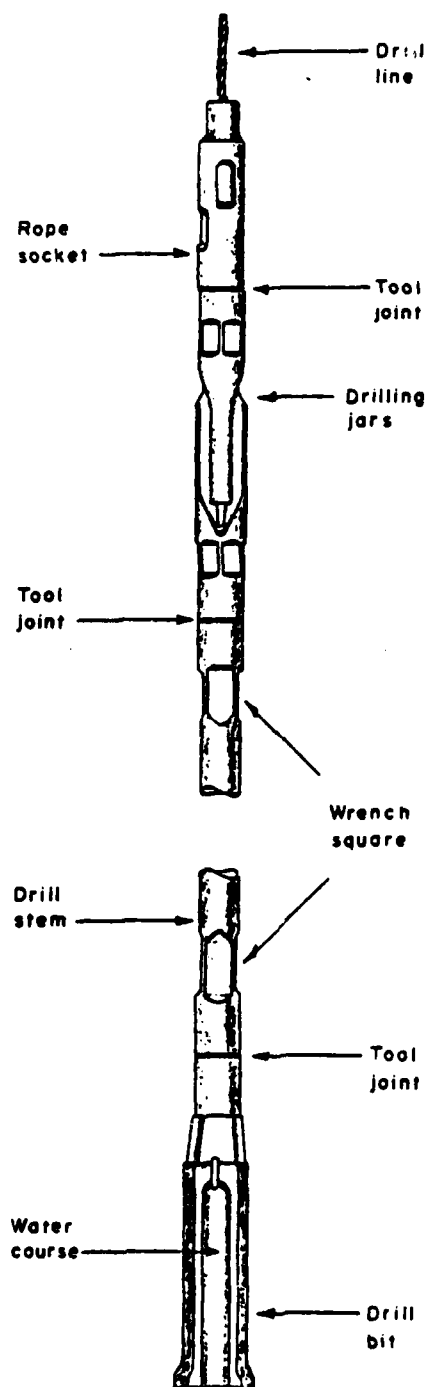


Figure 49. Four Components of the String of Drill Tools for Cable-tool Percussion Drilling.

Source: Johnson Division, Groundwater and Wells, UOP Inc., © 1982.

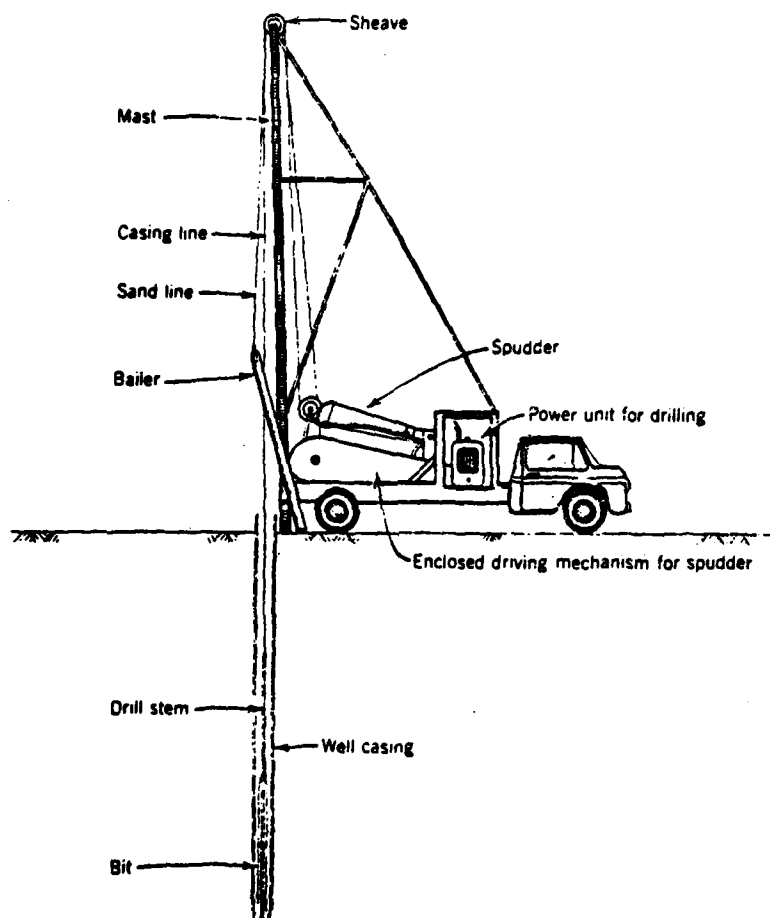


Figure 50. Truck-mounted Cable-tool Drilling Equipment.

Source: Davis, S.M. and R.J.M. DeWiest, Hydrogeology, John Wiley and Sons, Inc., © 1966.

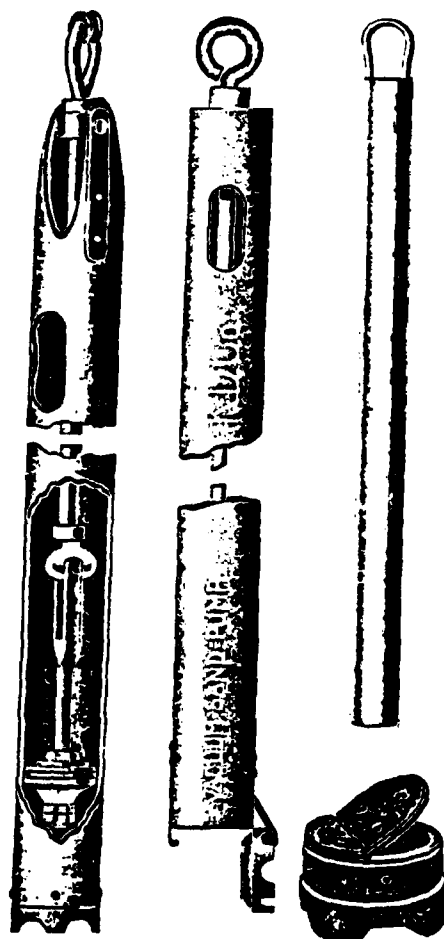


Figure 51. Sand Pumps and Regular Bailer used During Cable-tool Drilling.

Source: Johnson Division, Groundwater and Wells, UOP, Inc., © 1982.

Advantages

Disadvantages

Core sampling is possible only if hollow-stemmed auger flights are used.

Can be used only in unconsolidated sediments or soft rock.

Borehole will collapse in cohesionless sediment (sand and gravel).

Often impossible to use in soils below the water table.

b. Cable-Tool Percussion Drilling

Regular lifting and dropping (percussive action) of a heavy string of tools (cable-tools) deepens a hole being drilled with cable-tool equipment. A chisel-shaped bit on the end of the drill string breaks or crushes hard rock into small fragments or loosens unconsolidated sediments. The vertical motion of the drill string mixes the crushed or loosened particles with water to form a slurry. If no water is present in the formation being penetrated water must be added to form the slurry. When water-bearing formations are penetrated, they must be cased or grouted in order to deepen the hole (USEPA, 1980b).

Figure 49 shows all the components of a string of cable tools - a rope socket, a set of jars (to aid in loosening tools stuck in a hole), a drill stem (for weight and length), and a drilling bit (Walton, 1970). The drilling rig (Figure 50) for the cable-tool method consists of a mast, a multiline hoist, and an engine usually mounted on a truck (Davis and DeWiest, 1966).

After about 4 to 5 feet of drilling, the crushing action of the bit becomes impeded by the accumulation of the cuttings. At this point, the bit is removed from the hole and a bailer (Figure 51) is "allowed to fall to the bottom of the hole where it strikes the water, causing a rapid surge of water and cuttings upward within it" (Walton, 1970). The bailer is then withdrawn from the hole with the cuttings.

In unconsolidated formations, casings should be driven into the bottom of the hole to avoid caving (Todd, 1959). In formations prone to caving, unconsolidated sand and gravel, this method is least effective. This approach is best in consolidated rock such as limestone and sandstone. It is not capable of drilling as quickly or as deeply as rotary methods.

The cumulative summary of advantages and disadvantages of the cable-tool percussion drilling methods has been gathered from EPA, (1980b), Todd, (1959) Walton, (1973), and Campbell and Lehr, (1973).

Cable-Tool Drilling

Advantages

Simple equipment and operation.

Good seal between casing and formation if flush joint casing is used.

Good disturbed soil samples. Known depth from which cuttings are bailed.

Core samples can be collected.

If casing can be bailed dry without sand heaves, a formation-water sample can be collected.

Can be used in unconsolidated sediments and consolidated rocks.

Only small amounts of water are required for drilling.

Once water is encountered, changes in static or potentiometric levels are readily observable.

Suitable for rugged terrain.

Low initial investment in equipment.

Disadvantages

Slow.

Use of water during drilling can dilute formation water.

Potential difficulty in unconsolidated sand gravel.

No formation water samples can be taken during drilling unless open-ended casing is pumped, or a screen set.

Heavy steel drive pipe is used and could be subject to corrosion under adverse contaminant characteristics.

Cannot run a complete suite of geophysical well logs because of casing.

c. Hydraulic Rotary Drilling

Figure 52 illustrates the equipment used for hydraulic rotary drilling consisting of a derrick, or mast, a rotating table, a pump for drilling mud, a hoist and the engine. The method is described simply in the Johnson Division Report (1972):

"Hydraulic rotary drilling consists of cutting a borehole by means of a rotating bit and removing the cuttings by continuous circulation of a drilling fluid as the bit

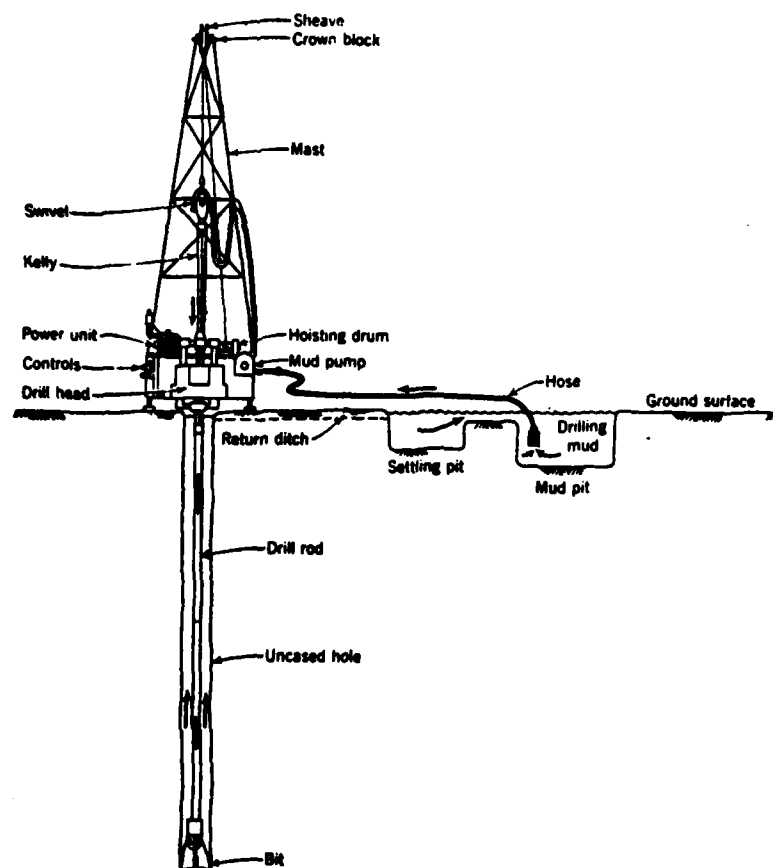


Figure 52. Major Components of Rotary Drilling Equipment. Arrows Indicate Direction of Mud Circulation.

Source: Davis, S.M. and R.J.M. DeWiest, Hydrogeology, John Wiley and Sons, Inc., © 1966.

penetrates the formation materials. The bit is attached to the lower end of a string of drill pipe. In the conventional rotary system, drilling fluid or drilling mud is pumped down through the drill pipe and out through nozzles in the bit. The mud fluid then flows upward in the annular space around the drill pipe to the surface, with the cuttings carried in suspension. At the surface, the fluid is channeled into a settling pit and then into a storage pit. It is again picked up by the pump after dropping the bulk of its load of cuttings."

The direct rotary drilling method is heavily dependent on fluid circulated through the hole during drilling (Figure 52). The fluid is generally drilling mud (bentonitic clay mixed in water), and it contributes to the hole stability by coating the hole (Freeze and Cherry, 1979). When even heavy drilling mud does not stabilize the hole, casing must be emplaced (as in the other drilling methods) for drilling to continue. The most common drilling problems encountered with this method are caving, lost circulation, and artesian water flowing into the hole.

Overall, the various rotary rigs are the fastest and most convenient means of drilling, especially in unconsolidated sediments. The list of advantages and disadvantages has been compiled from EPA (1980b), Johnson Division (1972), Freeze and Cherry (1979), and Todd (1959).

Hydraulic Rotary Drilling

Advantages

Fast.

Dilution of formation water is limited by formation of a filter cake on borehole walls.

Formation water sample can be obtained with a special technique.

Good disturbed soil samples from known depths if travel time of borehole cuttings is taken into account, although sorting may occur.

Disadvantages

Expensive.

Requires complex equipment and operation.

There is a potential for vertical movement in formation stabilizer material placed between casing and borehole wall after completion.

Advantages

Flexibility in final well construction.

Can run a complete suite of geophysical well logs.

Core samples can be collected.

Can be used in unconsolidated sediments and consolidated rocks.

Disadvantages

d. Sampling

Sediment samples can be obtained during any of these boring or drilling procedures. The two types of samplers used most frequently are the split-spoon samplers and coring samplers. At regularly spaced intervals and at every change in sediment or rock type a sample is collected by either method to document all subsurface lithologies.

The split-spoon sampler (Figure 53) consists of a thick-walled steel tube split lengthwise (Sowers, 1970). A cutting shoe is attached to the end lowered into the hole first. This shoe penetrates the sediment and prevents the sediment from falling back out of the tube. Samples can be collected using this tool in most unconsolidated sediments (except gravel) and even soft rock (Sowers, 1970).

For collecting samples in consolidated formations a sampling method known as coring is required. Coring is basically a method of drilling during which a sample is obtained. Cores collected as samples are between 4 and 30 inches in diameter and about 10 feet in length (Campbell and Lehr, 1973).

Double tube core barrels with an upper core-catcher assembly with spring fingers and a lower catcher with a spring activated pivoted attachment behind the drill bit are a common type of core barrel (Campbell and Lehr, 1973). Figure 54 shows an example of a simple core barrel.

The sampling procedure takes place during drilling where the core barrel and bit rotate while water or thin drilling mud are forced down the barrel and into the bit under high pressure. This pressure forces the rock core upward into the barrel where the lower cone-catcher assembly prevents it from falling back out (Sowers, 1970). This method of sampling does not work well in unconsolidated sediments or in decomposed rock. However, when used, it yields a continuous record of subsurface formations.

2. MONITORING WELL CONSTRUCTION

In hydrogeologic investigations of groundwater contamination incidents, monitoring wells are frequently used for sampling. A number

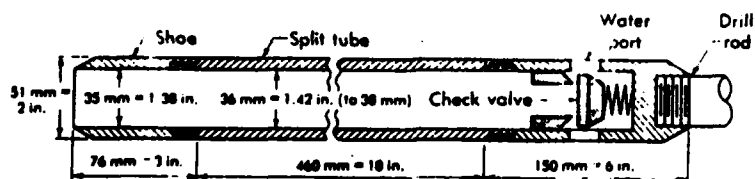


Figure 53. Standard Split-Spoon Sampler.

Source: Sowers, G.F., Soil Mechanics and Foundations: Geotechnical Engineering, Macmillan Publishing Company, New York, © 1970.

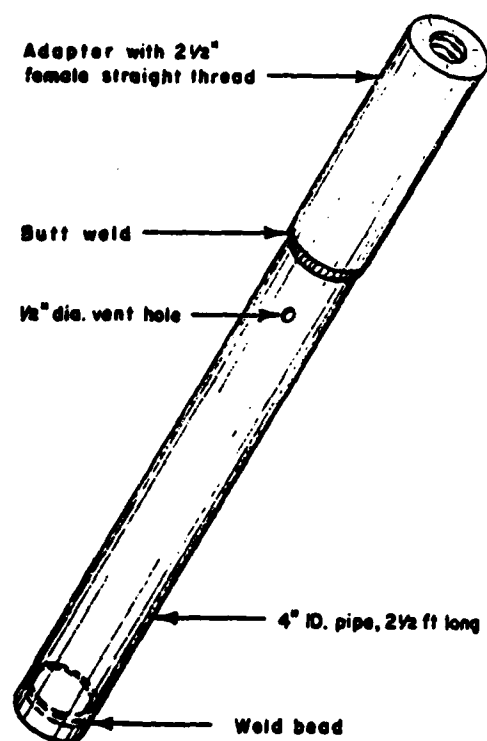


Figure 54. A Small Diameter Core Barrel
Suitable for Coring Inside
6-Inch Pipe

Source: Campbell, M.D. and J.H. Lehr, Water Well Technology,
McGraw-Hill Book Company, New York, © 1973.

of well configurations have been designed to meet the varied sampling needs and evaluate the most effective monitoring configurations.

The sampling design used in a monitoring well depends upon the objective of the monitoring program. Groundwater quality monitoring is usually done to determine what has already happened at an existing site, to provide a warning of what is starting or may start to happen, or to provide a baseline description. The most important consideration is establishing the vertical interval to be sampled. Generally, monitoring wells can provide two types of samples: depth-integrated samples, and point-source samples. With the depth-integrated approach, samples are drawn from wells or piezometers with long screens. With the point-sample approach, water samples are drawn from discrete levels in the groundwater zone. Each has its relative merits depending on the monitoring objectives.

The most popular monitoring well designs used to accomplish groundwater sampling are: (1) a single well, screened or open over a single vertical interval; (2) well clusters; (3) a single well with multiple sampling points; and (4) sampling during drilling. A discussion of each of these methods follows.

According to the EPA (1980b), "wells screened over a single vertical section of an aquifer are the most common construction method used to obtain groundwater samples from unconsolidated sediments or semi-consolidated rocks." (Figure 55) This type of design involves depth-integrated sampling. In consolidated rocks, the same effect can be obtained by sampling from an uncased hole. When the sampling interval includes the entire thickness of the aquifer, this method can aid in evaluating the areal distribution of aquifer contamination. However, data accuracy would decrease significantly in a study made on a smaller interval, since contamination distribution may not be uniform within the aquifer. The entire plume might not be sampled. A limitation of this type of well is that the vertical distribution of contaminant cannot be studied using depth-integrated sampling. In this type of sampling, the connate water may mask contamination or dilute the concentration of the contaminant. A single screen well is effective in studying areal extent of contamination when the sampling interval includes the entire aquifer. The data can then be used to plan more sophisticated monitoring wells. This sampling can also be useful when taking point-source samples over a short interval. However, depth-integrated sampling over a short interval provides incomplete data.

Wells with multiple sampling points overcome the dilution and vertical sampling problems of single-screen wells. Figure 56 illustrates some of the alternatives available. One of these alternatives is to cluster a number of single-screen wells. Such clusters consist of closely spaced, small-diameter wells completed at different depths (Figure 57). According to the EPA (1980b) "well clusters are by far the most common and successful technique to date for delineating groundwater contamination." The limitation that remains however is that there will always be an unsampled interval using this

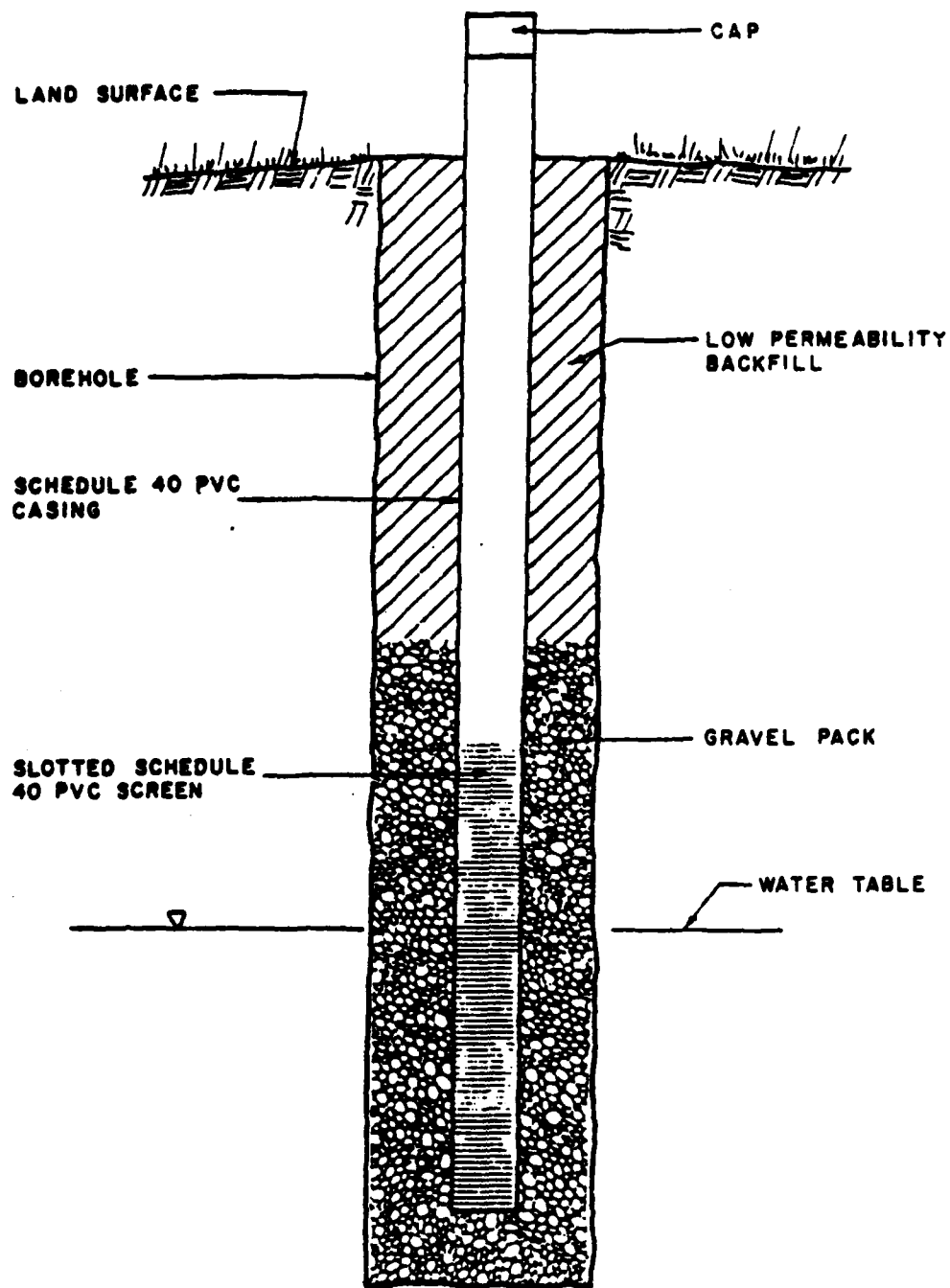


Figure 55. Typical Monitoring Well Screened Over a Single Vertical Interval.

Source: EPA, 1980b.

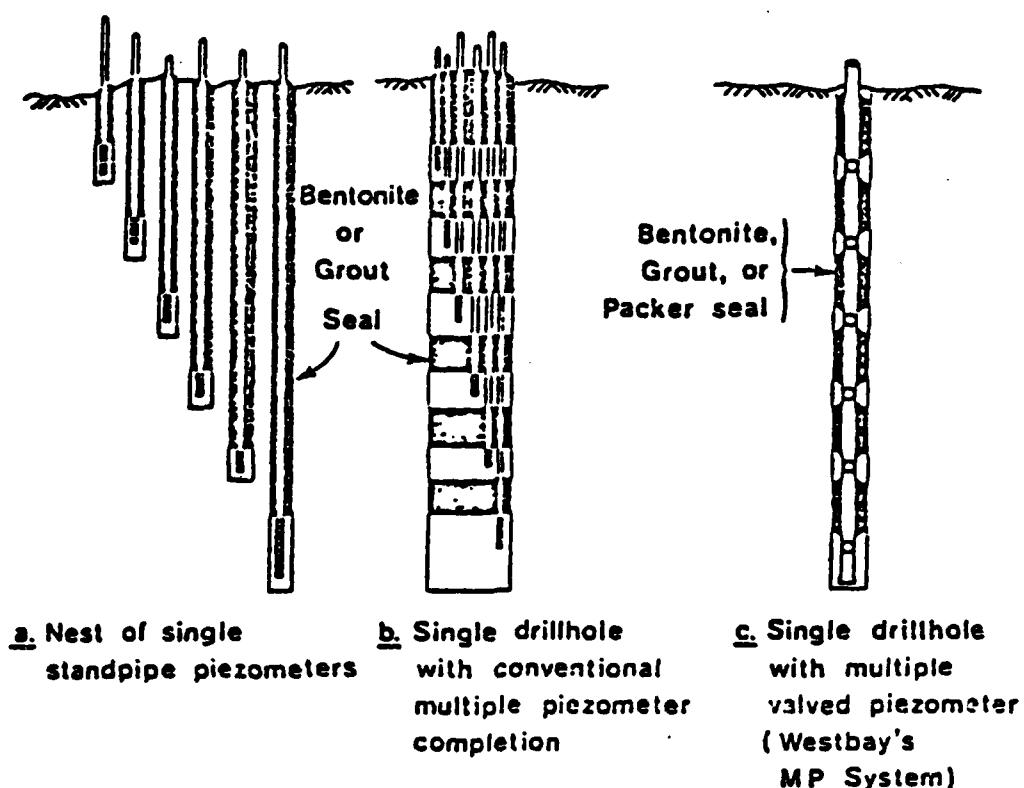


Figure 56. Examples of Piezometer Configurations for Groundwater Monitoring at Numerous Depths at a Site.

Source: Cherry, 1981.

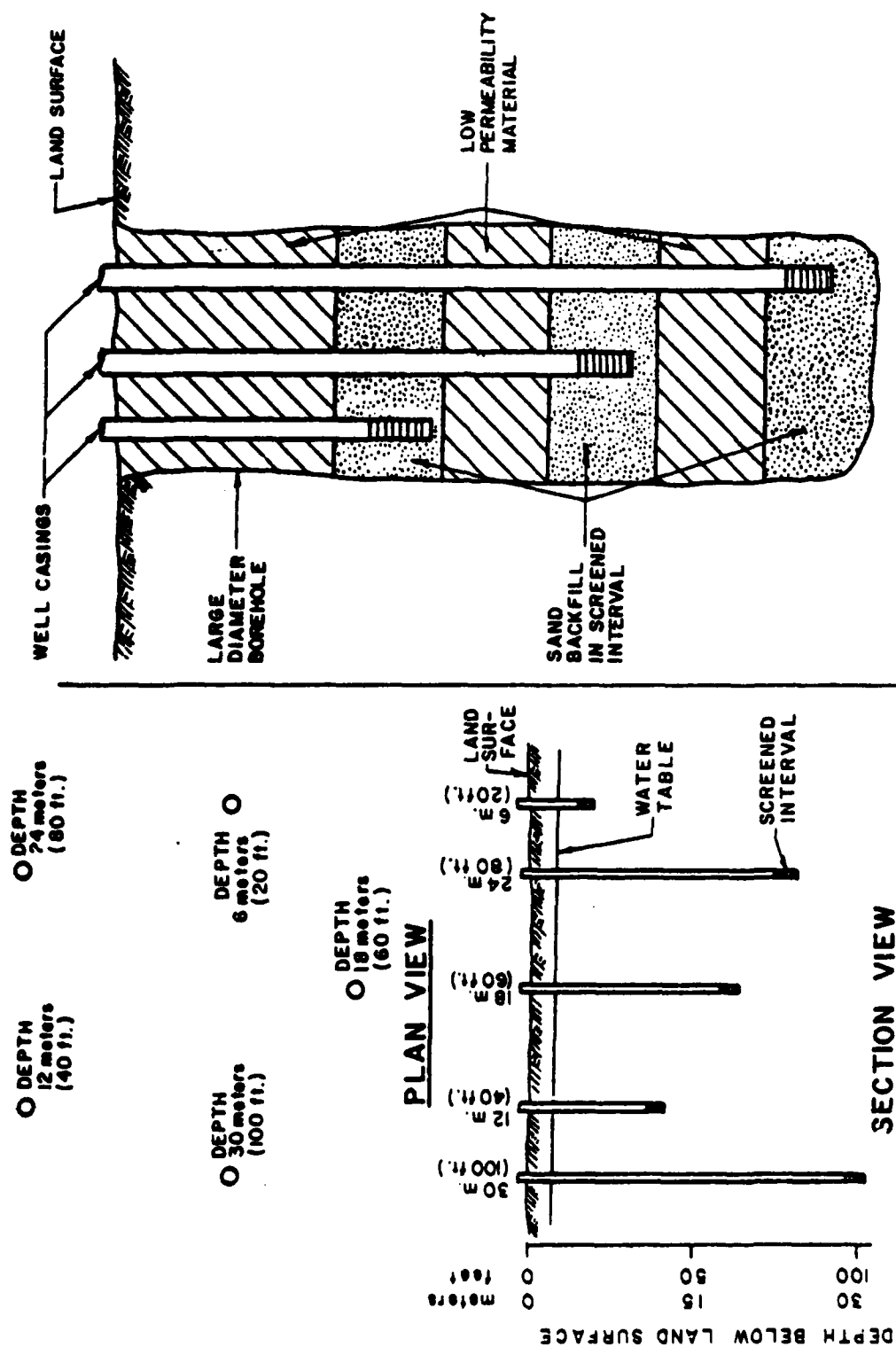


Figure 57. Typical Well Cluster Configurations

Source: EPA, 1980 b

technique. For this reason, completion depths should be carefully planned to maximize exposure. The EPA (1980b) lists several approaches to selecting depths:

- "a pair of wells, one screened at the top and the other at the bottom of the aquifer;
- a three-well cluster with screens set on the top, middle and bottom of the aquifer under investigation,
- clusters in which the screened intervals are separated by preselected intervals, such as:
 - the 3-, 6-, 9-, 12-, and 18-meter (10-, 20-, 30-, 40-, and 60-foot) screen depths;
 - the 6-meter (20-foot) separation from 6 to 30 meters (20-100 feet);
 - terminating 2 to 3 wells at 3 to 4.5 meters (10 to 15 foot) intervals."

Finally, the EPA (1980b) provides this insight into the use of well clusters:

"Some uncertainty will always exist as to the actual vertical distribution of the contaminant. Construction of more wells per cluster is not the answer; only a limited number of wells can be constructed close enough together to delineate vertical contaminant distribution at one particular point. Also, construction costs and the time required to complete the cluster would become prohibitive factors. The only way to obtain the most complete picture of leachate distribution is to collect groundwater samples during drilling."

Another method to obtain multiple sample points involves setting screens or casing perforations at intervals within a single borehole. Figure 58 illustrates a bundle piezometer and a multilevel point sampler which can be used in this type of operation. Vertical spacing of the sampling points depends on the data needs and the funds available for the particular investigation. In general, cost increases as the number of sampling points increases. When using this technology it is important to ensure the isolation of each sample point from the others. There can be no communication between intervals or unreliable samples will result. To accomplish this isolation, the sampling intervals are usually separated by packers of grout or bentonite. Besides careful packer placement, this configuration requires low pumping rates. This ensures that the samples are drawn only from the screened horizon, with

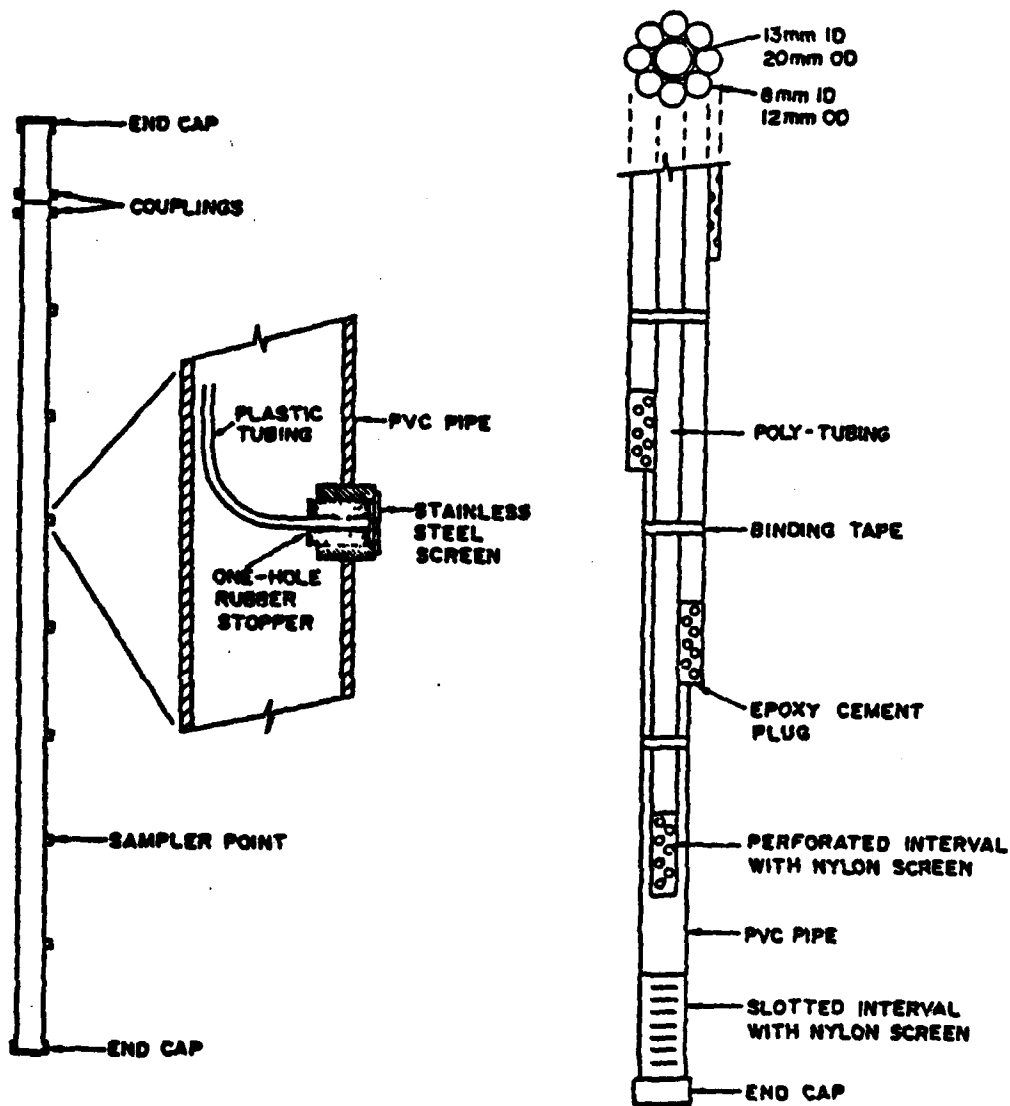


Figure 58. Two Multilevel Sampling Devices for Monitoring of Groundwater Quality in Cohesionless Deposits Below the Water Table.

Source: Cherry, 1981.

no vertical warping. Otherwise, an unrepresentative sample would be taken. With this technique, as with well clusters, however, there will be an unsampled interval. This problem actually turns out to be a major drawback because stratification of contamination within an aquifer is a common phenomenon. If sampling depths are not chosen carefully to intersect these zones, the vertical distribution obtained will be erroneous. Sampling during drilling can help overcome this problem of fixed point sampling of the other multisample methods. Figure 59 illustrates the configuration for sampling while drilling. This has been a very effective technique as long as precautions are taken to prevent contaminating the sample with drilling fluids and mud which would ruin the accuracy of the data. According to the EPA (1980b), "the main advantage of this type of sampling is that the stratification of contaminated slug can be defined with reasonable accuracy prior to setting a permanent casing and screen. With this information, the well can be designed for the most advantageous sampling or withdrawal of contaminant at that point in the aquifer. Changes in the vertical distribution can then be monitored closely."

3. GEOPHYSICAL TECHNIQUES APPLICABLE TO GROUNDWATER INVESTIGATIONS

a. Introduction

Geophysical techniques are directly applicable to groundwater movement and pollution investigations in several important respects:

- Surface geophysics are customarily used for an initial nondestructive, general site survey in order to describe the geologic framework and to help define the extent of a groundwater contamination problem in a cost-effective manner.
- Certain higher resolution surface geophysical methods (cf. metal detection) can be used to locate buried waste drums and, thus, pinpoint sources of contamination.
- Based on the interpretation of surface-geophysical data, the optimal location for drilling observation and monitoring wells can be determined.
- Borehole geophysical logging techniques should then be used to confirm, refine, and calibrate the interpretation of surface geophysical data. These techniques permit direct measurements of fluid flow and chemistry and, thus, an evaluation of the nature and extent of the pollution problem. In-situ sampling and monitoring programs can then be formulated.
- Finally, the geophysical data set provides spatially and temporally continuous information which

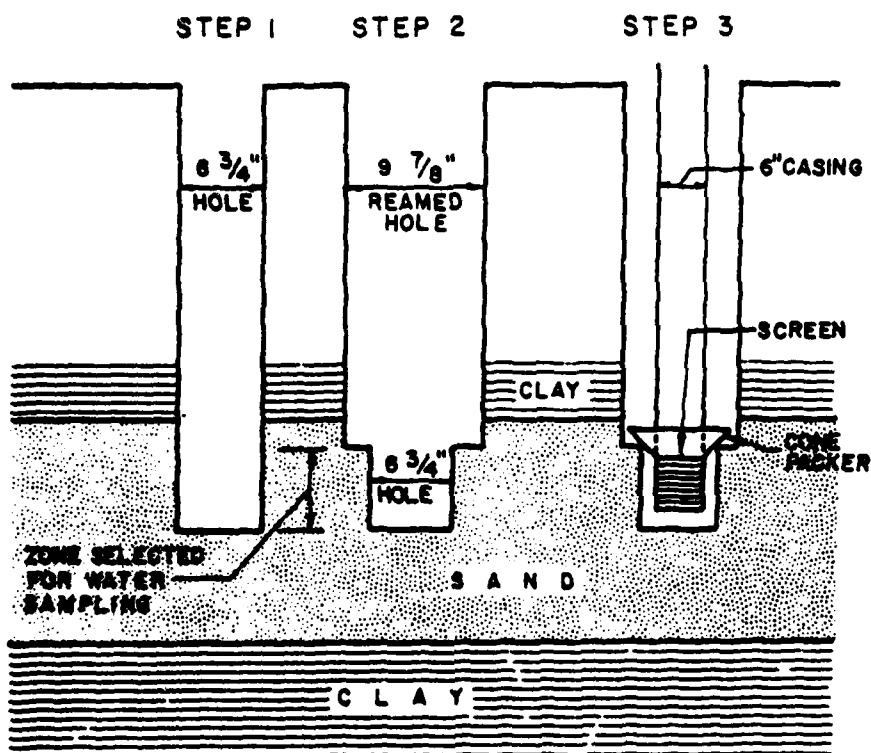


Figure 59. Procedure for Water Sampling During Drilling.

Source: EPA, 1980b.

complements discrete sets of laboratory measurements. Models of pollutant identity and migration in groundwater are severely constrained by geophysical and geochemical data derived from field surface and borehole measurements. Hence, confidence in model predictions is bolstered by field geophysics and laboratory testing.

In addition, the geophysical field investigations can be used to support test drilling:

- Borehole geophysical logging provides for lithologic sections and rock property analysis as well as for borehole cross-correlations between geologic strata.
- Surface geophysics can be used to supplement and extrapolate test drilling information after calibration against driller's logs.

The limitations inherent in the use of surface and borehole geophysics are discussed here in general terms. Organic contaminants, such as solvents, petroleum distillates, pesticides, and herbicides can change the properties of the pore fluid and matrix geology in several general ways:

- act as low-solubility, immiscible fluids, thus coating the grains and plugging the natural porosity;
- cause precipitation of certain complexing ions in formation waters, thus decreasing their activity in solution and the total dissolved solids (TDS) concentration;
- act as polar or ionic components, thus affecting the pH and Eh of groundwater and changing its electrical conductivity (resistivity).

These mechanisms must be identified, understood, and calibrated by laboratory and field testing for suspected contaminants before interpreting geophysical data. If a field resistivity anomaly of a certain porous or waterbearing formation is to be ascribed with confidence to organic pollution, calibration of in-situ natural characteristics is necessary. Seasonal fluctuations of water table levels at various locations and the degree of variation in porosity and saturation of unpolluted formations must be assessed with geophysical techniques before inferring the presence and effects of organic pollutants on the natural system.

b. Surface Geophysical Survey Methods

Surface geophysical methods are used widely for a nondestructive and cost-effective initial survey and assessment of potentially contaminated sites. The survey can be carried out by airborne instrumentation, flown on gridded patterns, for gross resolution; or by ground-based portable equipment, for finer-scale information. The standard techniques fall within the following main categories:

- gravity surveys
- magnetic surveys
- electrical conduction
- electromagnetic induction
- elastic wave or acoustic sounding techniques such as seismic reflection and refraction.

Those geophysical methods based on potential theory (gravity, magnetic or electrical) lack unique source solutions and require the combined use and correlation of several sounding curves, and borehole calibrations and sampling, to insure correct interpretation of results. The principles of geophysical survey methods are discussed in detail in the textbooks of Grant and West (1965) and Telford et al. (1976).

Several techniques applicable to the study of groundwater pollution are briefly discussed and illustrated with examples. The relative merits and disadvantages of the most widely used geophysical survey methods in groundwater studies are compared in Table 18.

(1) Gravity Surveying

Gravity survey field work consists of measuring the gravitational acceleration ($g = 980 \text{ gals} = 980 \text{ cm/sec}^2$) at grid stations covering the area of interest. Corrections for topography, latitude, elevation and earth tides must be applied, with respect to a local reference equipotential surface. Lateral variations in density give rise to a Bouguer gravity anomaly, which is the significant datum at each station. However, an interpretation of Bouguer gravity profiles (in milligals) is ambiguous in the sense that the shape, size and depth of the anomaly source is nonunique. Sensitive gravimeters or gradiometers require calibration and drift corrections to achieve practical sensitivities of 0.01 mgal. Since the gravitational acceleration varies inversely with distance squared, finer grid spacings are needed to resolve shallow anomalies. Ground surveys by a three- to four-person team are needed for accurate contouring of anomalies which have a positive sign for excess buried mass and a negative sign for low density, water-filled sedimentary formations. The interpretation of gravity residuals from regional gravity trends and contours requires use of graphical techniques, analytical models and computer analysis. To insure a correct interpretation, the true depth of strata and their respective densities must be determined from test drilling and sampling. The

TABLE 18. COMPARISON OF REMOTE SENSING TECHNIQUES

<u>Technique</u>	<u>Purpose</u>	<u>Advantages</u>	<u>Limitations</u>
<u>Electrical Resistivity</u> Lateral Profiling	<ul style="list-style-type: none"> • determine lateral extent of contaminated ground water • facilitate placement of monitoring wells and optimize their number • monitor changes in plume position and direction 	<ul style="list-style-type: none"> • procedure less expensive than drilling • procedure more rapid than drilling • equipment light-weight, able to be hand-carried • survey may be conducted in vegetated areas 	<ul style="list-style-type: none"> • limited ability to detect non-conductive pollutants • technique unsuitable if no sharp contrast between contaminated and natural ground water • interpretation difficult if water table is deep • interpretation difficult if lateral variations in stratigraphy exist • interpretation difficult if radical changes in topography are not accounted for in choice of A-spacing • technique unsuitable in paved areas or areas of buried conductive objects
Depth Profiling	<ul style="list-style-type: none"> • indicate change in contamination with depth • establish vertical control in areas of complex stratigraphy 	same as above	same as above
<u>Seismic Refraction</u> (non-explosive method)	<ul style="list-style-type: none"> • determine depth and topography of bedrock • determine depth of trench containing buried drums 	<ul style="list-style-type: none"> • procedure less expensive and safer than coring or excavation • procedure more rapid than coring or excavation • survey may be conducted in vegetated areas 	<ul style="list-style-type: none"> • technique unsuitable if no sharp velocity contrast between units of interest (e.g., trench containing buried drums and surrounding soil) • survey requires access road for vehicle • depth of penetration varies with strength of energy source • low velocity unit obscured by overlying high velocity units • interpretation difficult in regions of complex stratigraphy
<u>Metal Detection</u>	<ul style="list-style-type: none"> • locate areas of high metal content (e.g., buried drums) 	<ul style="list-style-type: none"> • procedure less expensive and safer than excavation or radar • procedure more rapid than excavation or radar • equipment light-weight, able to be hand-carried • survey may be conducted in vegetated areas 	<ul style="list-style-type: none"> • technique unsuitable for the detection of non-metallic objects • technique unsuitable for objects below five feet • technique unsuitable for determination of number or arrangement of buried objects
<u>Ground-Penetration Radar</u>	<ul style="list-style-type: none"> • locate buried objects (e.g., buried drums) • provide qualitative information regarding drum density • detect interfaces between disturbed and undisturbed soil (e.g., bottom of trenches) • detect plumes of high chemical concentration 	<ul style="list-style-type: none"> • procedure less expensive and safer than excavation • procedure more rapid than excavation • procedure deeper-penetrating than metal detection • procedure yields more information than metal detection • procedure may be used over paved areas 	<ul style="list-style-type: none"> • technique unsuitable for vegetated areas • data requires sophisticated interpretation • underlying objects obscured by those above • survey requires access road for vehicle

Source: Kolmer, 1981

idealization required for modeling a complex field situation limits the utility of gravity surveys. However, as Figure 60 illustrates, the technique is useful in identifying porous, permeable strata such as buried stream channels and unconsolidated sedimentary formations, as well as permit estimates of depth to the water table.

(2) Magnetic Surveys

Magnetic surveys permit the detection and delineation of buried metallic objects, such as barrels (see (6) below) and of geological anomalies such as hydrothermal ore deposits, magnetic mineral formations and buried mafic plutons with sufficient magnetic contrast to surrounding rock. The magnetic signal intensity at the detector depends on the type and contents of magnetic minerals present, the depth of the anomalous body (since the dipole magnetic field strength decreases steeply as the inverse cube of the depth of the source) and its size and geometry. The total field intensity has contributions from the ambient earth's field, the induced moment of the anomaly and its intrinsic magnetic remanence.

Thus, in field measurements, the background earth's field (0.5 oersted = $50,000 \gamma$) is subtracted from the total field strength, measured by portable instruments such as flux gate, nuclear precession or rubidium vapor (optical pump) magnetometers. Magnetic variometers or gradiometers achieve greater sensitivity ($10 - 20 \gamma$) and measure differential changes in the magnetic field, rather than its total intensity.

Airborne magnetic (aeromagnetic) mapping requires repeated measurements, towed or fixed sensitive instruments in gridded patterns. For interpretation of magnetic profiles, a number of corrections are necessary for anomalous signals weaker than approximately 500γ ; for nearby magnetic objects (railroad tracks); background drift due to diurnal field variations, and topography. Field anomalies are matched to simple geometrical shapes, at model depths and of model compositions. The same ambiguities in source characterization exist as in the case of gravity surveys. Ground-truth sampling and laboratory testing is needed to verify each interpretation. Figure 61 shows a way to combine gravity and magnetic measurements for more accurate interpretation.

(3) Electrical (Resistivity) Surveys

One of the most useful surface survey methods in groundwater studies is based on measuring the electrical resistivity (or its inverse, the conductivity) of ground layers. Each class of rocks has a characteristic range of values and within each class the degree of saturation with pore water and the pore fluid composition (cf. ionic concentration) lead to systematic variations in its conductivity. Resistivity surveys have been successful in locating the water table, mapping buried stream channels and detecting clay strata (Figures 62 and 63). Electrical surveys provide information on subsurface geologic

APPLICATION OF SURFACE GEOPHYSICS

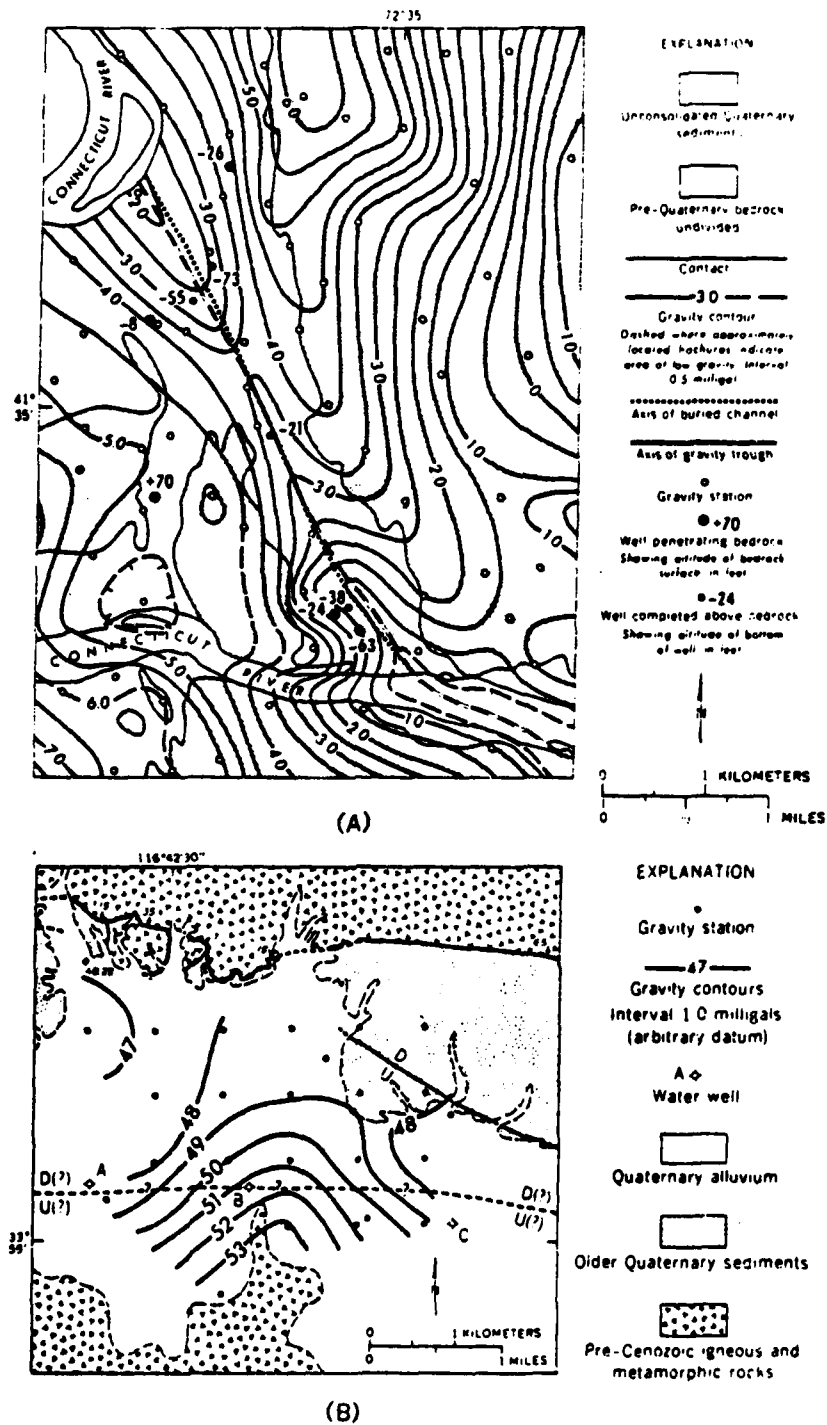


Figure 6C. (1) Complete Bouguer-Gravity Map of a Buried Pre-Glacial Channel of the Connecticut River. (2) Complete Bouguer-Gravity Map of San Gorgonio Pass, California

Source: Zohdy, et al., 1974.

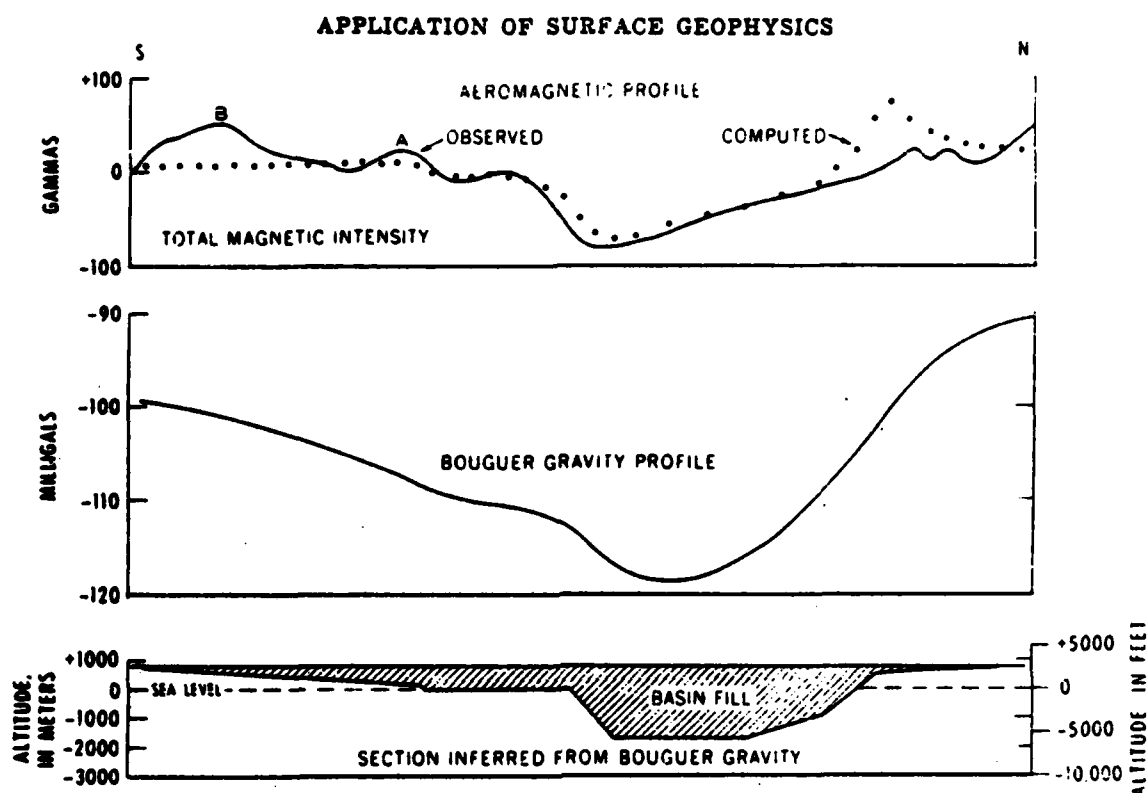


Figure 61. Gravity and Aeromagnetic Profiles Across Cenozoic Basin in Antelope Valley, Calif. Aeromagnetic Profile Flown at 150 meters (500 Feet) Above Ground Level

Source: Zohdy et al., 1974.

TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

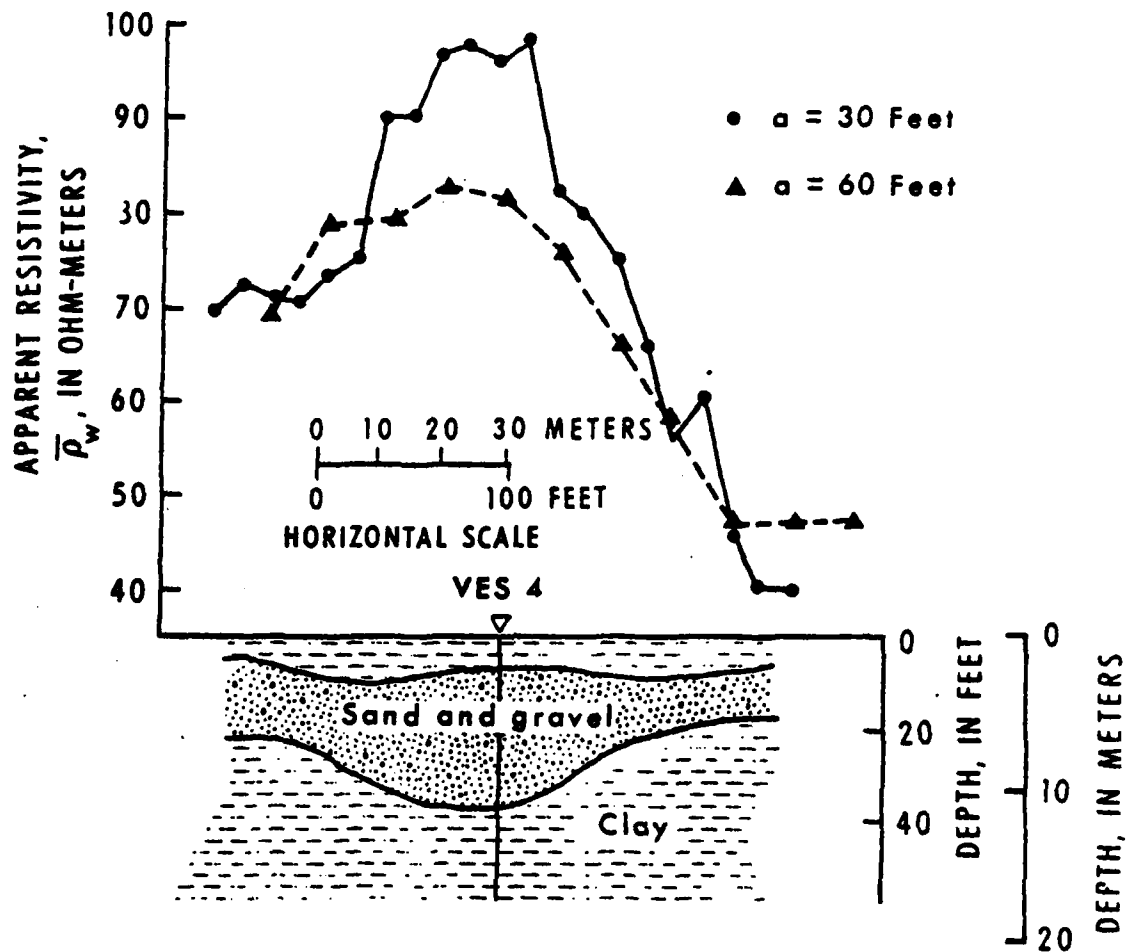


Figure 62. Horizontal Profiles over a Buried Stream Channel Using Two Electrode Spacings: $a = 9.15$ Meters (30 feet) and $a = 18.3$ Meters (60 Feet). VES 4 Marks the Location of an Electrical Sounding Used to Aid in the Interpretation of the Profiles

Source: Zohdy et al., 1974.

APPLICATION OF SURFACE GEOPHYSICS

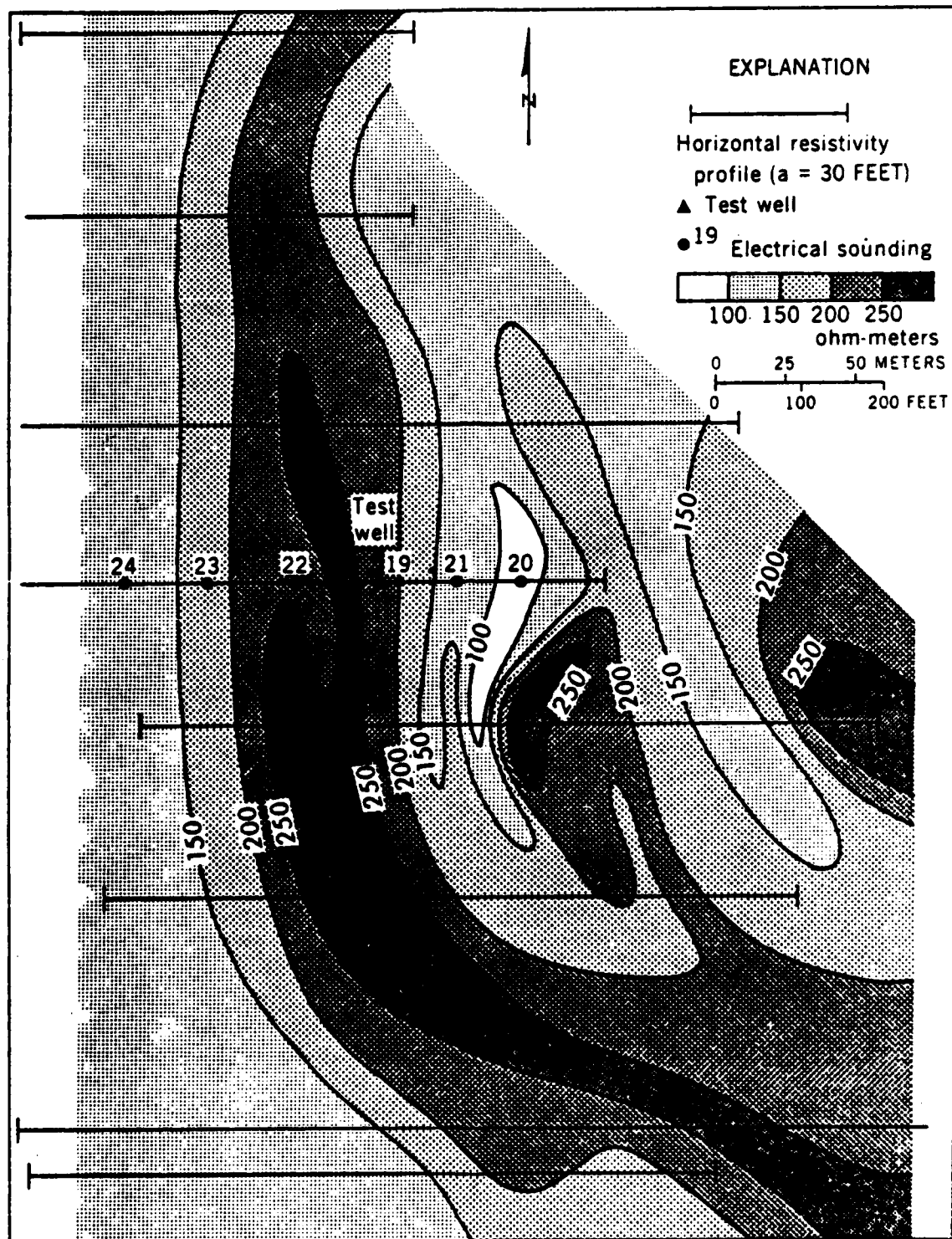


Figure 63. Apparent-Resistivity Map near Campbell, Calif. Unpublished Data Obtained by Zohdy (1964) Using Wenner Array. Crosshatched Areas are Buried Stream Channels Containing Thick Gravel Deposits. Stippled Areas are Gravelly Clay Deposits

Source: Zohdy et al., 1974.

features (such as the depth of a fresh/saline water interface or depth of a thick clay layer between two aquifers) which are not obtainable by gravimetric, magnetic or seismic survey methods. For surface resistivity measurements, metal electrodes are placed in the ground in various configurations (e.g., as Wenner, Schlumberger and Dipole-Dipole arrays) and the potential drop across two of them is measured directly. The current flow paths can be characterized by iso-resistivity contour maps (Figures 62 and 63) obtained by moving the electrodes between various stations, for lateral profiling at a given depth; or by numerous measurements at a given station at various depths, for depth sounding. Commonly, both horizontal profiling and depth electrical sounding techniques are combined to determine the presence, location and extent of permeable layers. However, interpretation of iso-resistivity maps or apparent resistivity profiles require either calibration and confirmation by borehole geologic and geophysical measurements or matching of modeling assumptions to computer predictions to optimize accuracy.

(4) Electromagnetic (EM) Methods

These depth sounding methods are best suited to detection of good electrical conductors at shallow depth. They encompass various methods involving the propagation of time-varying (continuous or pulsed) electromagnetic fields through the earth layers. An EM source (transmitter) introduces energy into the ground, inducing secondary currents and fields in the conducting body, which are detected by an antenna receiver at the surface.

One field method makes use of atmospheric signals resulting from worldwide thunderstorm activity (sferics) and detects induction responses as audio-frequency magnetic fields (AFMAG).

Other methods make use of very low frequency (VLF) (5 - 25 kHz) signals from fixed ground stations and yet others, of moving radio frequency (RF) signals in the frequency range 10 kHz - 10 MHz, to achieve a range of depth of penetration. The power frequency and distance characteristics of available systems are selected as appropriate to the field conditions and resolution desired. A great variety of transmitter loop-receiver coils configurations are practiced for ground and airborne surveys: long wire, two dipoles in phase or in quadrature, variable dip-angle systems in parallel or broad orientation along the traverse line, horizontal loop systems, rotary field systems for two aircraft, etc. In order to isolate a small secondary response from a larger primary signal, transient INPUT (Induced Pulse Transient) systems have been introduced for time-domain, rather than frequency-domain, operation. The INPUT airborne systems have greater penetration depth and afford better characterization of the conducting bodies. The height of the aircraft and transmitter-receiver separation control the sensitivity for a given system. Data interpretation requires theoretical modeling of conductor shape and sizes to match the response of conducting sheets, spheres, cylinders, or lines in uniform or dipole fields. For complex geometries and variable conductivity,

computer analysis of data is necessary. Table 19 summarizes the range of dielectrical constants and electrical conductivities for typical earth materials.

(5) Electrical Sounding Using Natural Sources


Several practical methods of deep electrical sounding take advantage of natural electric and electromagnetic phenomena and require only passive sensors and no power sources. These are:

- The Self-Potential (SP) Method which detects background potential drops due to fluid streaming through a formation, varying electrolyte concentration and changing electrochemical activity of groundwater. Regional gradients of 10 mV/1000 feet are typical of these sources (streaming potentials). Polarization potentials associated with mineralization zones give rise to SP anomalies of order < 200 mV. pH variations above and within the water table also contribute to current and potential flowing around conducting zones. Detection of SP voltage drop requires simple field equipment, basically a potentiometer and two electrodes. However, the data interpretation may be difficult.
- Telluric and Magnetotelluric Methods detect large scale current and low frequency magnetic fields induced in surface ground layers by atmospheric (ionospheric) currents. These vary diurnally and with latitude and are subject to high frequency fluctuations due to electric and magnetic storms. These methods are still under active development and require sensitive equipment and careful interpretation of field data, after subtracting the undistorted background fields from distortions due to the local geology. The techniques have been applied to deep sounding and large scale interpretation of basement rock structures.

(6) Metal Detectors

Metal detectors and magnetic sensors offer reasonable sensitivity and reliability to depths of approximately 5 feet. Metallic targets at or near the surface can be reliably detected with magnetic induction detectors, while magnetometers (total field flux gates and magnetic gradiometers) can "see" up to 5 feet depths. However, radar-type techniques are needed to penetrate down to 20 feet or more of ground cover. The penetration effectiveness of electromagnetic radiation (pulsed or continuous wave CW) depends on the power of the emitter/receiver system, on its frequency domain and on the attenuation properties of the ground cover and its contrast to the target. Ground penetrating radar (GPR) and other pulsed radio frequency (RF) systems are becoming more widely applied for detecting shallowly buried waste barrels, whether made of metal or plastic. Metal detectors are based on

TABLE 19. APPROXIMATE VHF ELECTROMAGNETIC PARAMETERS OF EARTH MATERIALS

Material	Approximate Conductivity (MHO/M)	Approximate Dielectric Constant	Depth of Penetration
Air	0	1	Max (km)
Limestone (Dry)	10^{-9}	7	
Granite (Dry)	10^{-8}	5	
Sand (Dry)	10^{-7} to 10^{-3}	4 to 6	
Bedded Salt	10^{-5} to 10^{-4}	3 to 6	
Fresh Water Ice	10^{-5} to 10^{-3}	4	
Permafrost	10^{-4} to 10^{-2}	4 to 8	
Sand, Saturated	10^{-4} to 10^{-2}	30	
Fresh Water	10^{-4} to 3×10^{-2}	81	
Silt, Saturated	10^{-3} to 10^{-2}	10	
Rich Agricultural Land	10^{-2}	15	
Clay, Saturated	10^{-1} to 1	8 to 12	
Sea Water	4	81	Min (cm)

Source: Arthur D. Little, 1980.

electromagnetic induction: AC currents in a surface coil give rise to a time-varying primary magnetic field at a metallic conductor and hence to induced eddy currents and a secondary magnetic field. This secondary magnetic field is then picked up at the surface with a coil connected to a sensitive electronic amplifier, meter or potentiometer bridge. The anomalous secondary field may be due to a metallic object or to a high-conductivity anomalous zone in the ground. Ordinarily, operating frequencies for EM induction prospecting instruments are ≤ 5 kHz, although they may reach 50 kHz.

(7) Ground Penetrating Radar

GPR systems, also more generally called pulsed RF, or impulse-radar systems, have been applied to detection of buried objects, rock cavities, faults and to locating the water table in different soil types. Pulsed RF systems have been operated in the frequency range of 1 to 6000 MHz, for maximum penetration depths of 225 to 3 meters, respectively.

The GPR uses pulsed transmission of electromagnetic signals and reflected target energy to detect the presence and depth of a target. The attenuation loss of the signal in the ground increases with ground conductivity and with frequency for a given material. A 10 dB loss indicates that only 1/10 of the energy survives passage through a given earth material. Depending on moisture content, attenuation to a given depth can vary from a fraction of dB/foot for dry soils up to 30 dB/foot in wet clay. The velocity (v) of propagation of radar in the ground is slower than in air (c), by the fraction

$$\frac{v}{c} = \frac{1}{\sqrt{\epsilon}}$$

where ϵ is the relative dielectric constant of the ground material (Table 19). For typical $\epsilon = 2$ -10, the radar wave ground velocity is 0.3 - 0.7 ft/nanosecond, so that signal round trip time delays are of order 10^{-8} seconds. The dielectric constant varies also with moisture content (percent saturation), as well as with mineralogical makeup (Table 19). Metal targets are near-perfect reflectors of radar energy and show a characteristic hyperbolic signature or profile radar charts.

A radar system developed by Geophysical Survey Systems, Inc. (GSSI) has been applied to profiling the ground to a maximum depth of 25 feet in sand and 5 feet in varved clays. This method is called Electromagnetic Subsurface Profiling (ESP) and has been used to detect buried pipes. The ESP system is a broad band videopulse radar, with variable gain, which generates graphic radar displays requiring careful interpretation in terms of frequency content and amplitude of the reflected signal, by a technique called Time-Domain Reflectometry (TDR). Interpretation of charts must be based on field calibrations and on laboratory and borehole information to minimize ambiguities. Several GSSI survey instruments are available (e.g., Models 3105 AP and 3102), operating at different center frequencies (e.g., 300 MHz and 600 MHz).

with different spatial resolution and penetration depth (which varies roughly as the inverse square of the frequency).

(8) Seismic Profiling

Seismic profiling is a relatively deep acoustical (elastic wave) sounding technique. Seismic energy from an explosive, vibrating (vibroiseis) or percussive (hammer) surface source is reflected from geological interfaces and discontinuities and detected by arrays of geophones. Continuous subsurface profiles can be obtained via a fixed array of detectors (geophones) distributed on the surface, or by gridded surface coverage from a moving vehicle. The geophones are transducers which convert the reflected acoustic signal to an electrical signal, which is subsequently amplified and recorded digitally on a magnetic tape or graphically on a strip chart recorder. The principles of geometrical ray optics are used for analyzing the propagation path of a spherical seismic wave from the source to the receiver. Both the frequency content and the amplitude of the reflected signal, as well as its time of arrival at the detector carry information on the homogeneity, depth, density contrast, porosity and fluid content of earth layers. The presence of pore fluid changes the sonic velocity and attenuation properties of a formation. The interpretation of reflected seismic data is complicated by the presence of refracted waves and by inelastic-attenuation losses (which increase with frequency), as well as by ambiguities in the number and homogeneity of reflecting layers (Figure 64).

The relative transmission and reflection coefficients and the vertical and lateral homogeneity of formations, i.e., anisotropy and the round-trip travel paths for the compressional (p-type or body) waves are interpreted in terms of "earth models" (Figures 64).

Logitudinal shear (S-type) seismic waves are sometimes more useful in detecting the depth of an aquifer or inferring pore water saturations, since they are severely attenuated by fluids. Also, seismic refraction methods are often useful in measuring the depth to the water table, since the zone of saturation acts as a strong refractor. There is usually sufficient velocity contrast between dry and saturated sediments (0.1 - 1 km/sec), to insure good resolution of wet zones from signal travel time differences. The acoustic velocity of refracted seismic waves is directly related to the density, porosity and saturation of rocks, in the geologic section.

(9) New Techniques and Instruments

Other new nondestructive geophysical techniques for applications to environmental assessments of hazardous waste sites include:

- Time-domain reflectometry (TDR) which has been used to map soil moisture content along buried transmission lines and breaches in landfill liners. TDR is analogous to a 1-D radar along a transmission

line and detects discontinuities along it. It requires the installation of buried parallel cables in the ground to monitor the wetness of a backfill or landfill.

- Acoustic-emission (AE) can be used to detect resaturation and fluid flow in soils and rocks, assuming that laboratory calibration data on seepage flow and fracture flow AE exist, to aid in interpretation of field data. This monitoring method requires installation of borehole hydrophones and surface geophones to "listen" to stress changes in rock due to fluid flow.

A recent trend towards more systematic geophysical data acquisition for less ambiguous interpretation has been to pair complementary techniques for mapping subsurface geological and geochemical features. For example, one can combine electrical resistivity (ER) with impulse radar (GPR), and use formation resistivities to assess the depth of penetration of radar pulses and use radar signatures for geological interpretation of ER results.

Another trend has been to integrate remote sensing techniques with direct environmental sampling programs, in order to reduce costs and optimize locations for the latter and to improve the accuracy of the former.

Recent advances in the remote sensing geophysical instrumentation have focused on portability, sensitivity and expanded data storage and processing capability:

- Electrical Methods: Both frequency-domain and time-domain electromagnetic (EM) systems were recently improved such as the airborne Pulse Electromagnetic (PEM) Crone System, the SIROTEM II System by GEOEX and the EM-37 System by Geonics. Improved ground systems include the Scintrex Genie time-domain EM system and new IPR-11 induced polarization spectral receiver; as well as the Phoenix new 100 kW 1P/R (induced polarization-resistivity) instrument and a real-time magnetotelluric (MT) device.
- Gravity and Magnetic Methods: airborne (helicopter) gravity surveys have recently achieved 0.5 milligal accuracies although on gridded flights the cost of surveying is high (approximately \$200/km). Both GeoMetrics and EDA have recently introduced proton-precession field magnetometers for total-field intensity measurements, with data storage and processing capabilities.

- **Seismic Methods:** the recent improvements have focused on higher resolution, greater recorder capability and higher speed data transfer. For example McSEIS-1500 (an OYO Instruments system) has a 24-channel recorder with digitized output to a floppy disk.

c. Borehole Geophysics

Borehole geophysical techniques are necessary for calibrating and verifying information derived from and the interpretation of surface geophysical surveys. Borehole logging, coring, and sampling methods provide vital information on the geologic context and distribution of liquid water and waste vs. depth. Geophysical well logging provide data on the location, thickness, and lateral continuity of waste-storage zones and the confining beds based on estimates of porosity and permeability. Other physical properties, lithologic boundaries, and structural discontinuities affecting the potential pollutant migration can also be determined. For example, by cross-plotting acoustic-velocity and neutron or gamma-gamma logs, one can discriminate between fracture vs. intergranular porosity. Also, the distribution and orientation of fractures can be determined by acoustic televiewer logs. By measuring the conductivity, temperature, viscosity, and density of interstitial fluids, logs can be used to infer the chemical nature of native and pollutant fluids. Logs can serve to monitor in-situ changes in the groundwater system, such as porosity changes due to plugging by immiscible organics, or precipitation of solutes after chemical treatment. Thus, a continuous borehole logging program can guide remedial action at a polluted site.

Geophysical well logging is necessary to measure and monitor fluid chemistry, density, and viscosity changes due to waste migration, to map the distribution of groundwater types, and to establish flow patterns and the distribution of pollutants relative to recharge area. The time-lapse technique compares well logs run at selected time intervals to detect the nature and extent of fluid changes.

Geophysical borehole logs are based mostly on in-hole, wire-line measuring techniques (Figure 65). These yield a set of continuous analog or digital records of physical or chemical parameters (Figure 66), which require interpretation in terms of lithology, geometry, resistivity, and formation factors; bulk density and porosity, permeability, and moisture content and composition, as well as yield of water-bearing formation. These parameters are often interrelated so that a redundant set of different measurement techniques is required to determine their value (Figure 66). The groundwater velocity is proportional to the product of the intrinsic permeability and hydraulic gradient and inversely related to the effective porosity. The porosity may be inferred from at least two types of neutron, gamma-gamma, resistivity, or acoustic velocity logs. The velocity of groundwater movement between two wells can be derived from radioactive tracer

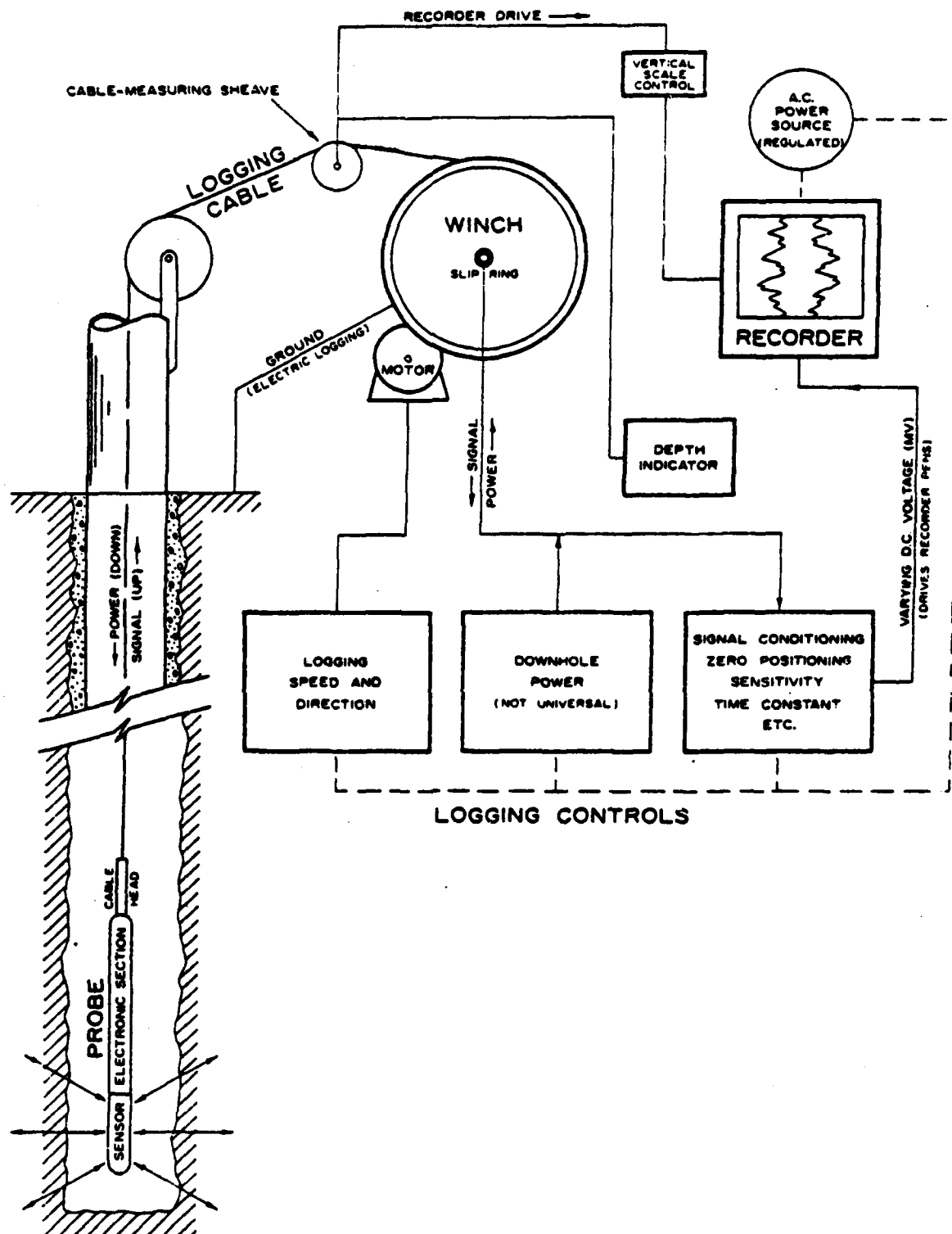


Figure 65. Schematic Block Diagram of Geophysical Well-Logging Equipment

Source: Keys and MacCary, 1971.

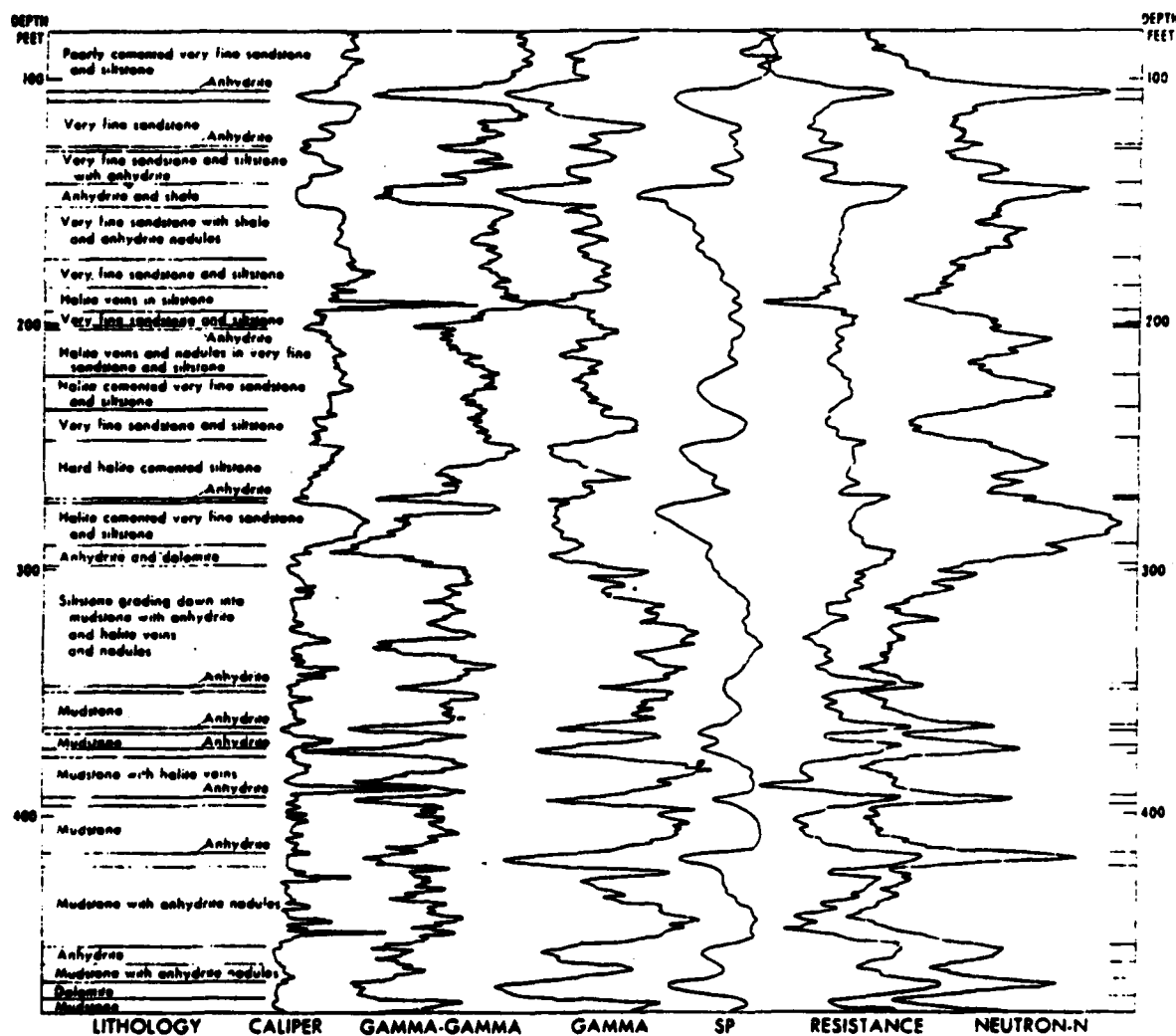


Figure 66. The Relationship of Six Different Geophysical Logs to Lithology, Upper River Basin, Texas.

Source: Keys and MacCary, 1971.

injection and migration tests detected by gamma emission. Hence, the intrinsic formation permeability can be estimated.

The basic well logs most widely correlated, based on calibrated crossplots, to permit more accurate and less ambiguous interpretation for surface mapping are listed in Table 20 and are briefly discussed in the text. Computer processing of log overlays or log combinations is often used for more complete interpretation.

The SARABAND technique is used for shaly-sands and water-bearing simple lithologies to determine water saturation and hydrocarbon weight and volume, together with bulk volume, porosity and permeability index analysis of the formation. SP, gamma-ray, and caliper logs are run in conjunction with one of the following log types: resistivity (Induction Log, Dual Induction Log, Laterolog, or Dual Laterolog); density (FDC - Formation Density Compensated Log); neutron (SNP - Sidewall Neutron Porosity or CNL - Dual Spacing Neutron logs); sonic (BHC - Borehole Compensated Log); microresistivity (proximity log or microlaterolog).

For complex lithologies, CORIBAND is used as a general interpretation code used in the oil-gas and exploration industries. Three to four types of logs are run to insure a minimum of ambiguity in output. Reference to standard crossplots is made in data reduction and statistical averaging of parameters is used.

The most widely used logging techniques and their areas of application are:

- (1) Natural gamma: measures natural radioactivity of borehole walls and detects changes in lithology.
- (2) Neutron-gamma: neutron bombardment coupled with gamma ray capture is used to detect changes in pore water concentration above the water table and, if calibrated, is a measure of porosity.
- (3) Gamma-gamma: gamma ray from a source is absorbed by the rock walls in direct proportion to their density.
- (4) Caliper: a record of the average diameter of a drill hole which helps to locate fractures, cavities, swelling of hydrated clays, dissolution of matrix by pore fluids, and unconsolidated wet sands.
- (5) Spontaneous Potential (SP)/Resistivity: is measured by several variants (normal, single-point, and focused-beam) (Table 21). They provide direct information on fluid chemistry, including total dissolved solids concentration and salinity (Figure 67). Correlative information for interpretation of the downhole mineralogical and zonation based on other logs is also obtained from electric logs. The

TABLE 20. SUMMARY OF LOG APPLICATIONS

Required information on the properties of rocks, fluid, wells, or the ground-water system	Widely available logging techniques which might be utilized
Lithology and stratigraphic correlation of aquifers and associated rocks.	Electric, sonic, or caliper logs made in open holes. Nuclear logs made in open or cased holes.
Total porosity or bulk density.....	Calibrated sonic logs in open holes calibrated neutron or gamma-gamma logs in open or cased holes.
Effective porosity or true resistivity.....	Calibrated long-normal resistivity logs.
Clay or shale content.....	Gamma logs.
Permeability.....	No direct measurement by logging. May be related to porosity, injectivity, sonic amplitude
Secondary permeability - Fractures, solution openings.	Caliper, sonic, or borehole televiwer or television logs.
Specific yield of unconfined aquifers	Calibrated neutron logs
Grain size.....	Possible relation to formation factor derived from electric logs.
Location of water level or saturated zones.	Electric, temperature or fluid conductivity in open hole or inside casing. Neutron or gamma-gamma logs in open hole or outside casing.
Moisture content.....	Calibrated neutron logs.
Infiltration.....	Time-interval neutron logs under special circumstances or radioactive tracers.
Direction, velocity, and path of groundwater flow.	Single-well tracer techniques - point dilution and single-well pulse. Multi-well tracer techniques.
Dispersion, dilution, and movement of waste.	Fluid conductivity and temperature logs for some radioactive wastes, fluid sampler.
Source and movement of water in a well.	Injectivity profile. Flowmeter or tracer logging during pumping or injection. Temperature logs.
Chemical and physical characteristics of water, including salinity, temperature, density, and viscosity.	Calibrated fluid conductivity and temperature in the well. Neutron chloride loggins outside casing. Multielectrode resistivity.
Determining construction of existing wells, diameter and position of casing, perforations, screens.	Gamma-gamma, caliper, collar, and perforation locator, borehole television.

Sources: Keys and McCary, 1971.

TABLE 21. HYDROLOGIC APPLICABILITY OF ELECTRIC LOGS

Properties to be investigated	Type of electric log								
	Single point	Short normal	Long normal	Lateral device	Wall resistivity (nonfocused)	Focused guard and laterolog	Micro-induction	Induction	SP
Lithologic correlation.....	X	X	X	X	X
Bed thickness.....	X	X	X	X	X	X	X
Formation resistivity (low R muds).....	X	X	X	X
Formation resistivity (fresh mud).....	X	X	X
Invaded zone resistivity.....	X
Flushed zone resistivity.....	X	X
Mud resistivity ¹ (in place in hole)....	X
Formation water resistivity.....	X	X	X

¹Use mud kit for pit samples.

Source: Keys and McCary, 1971.

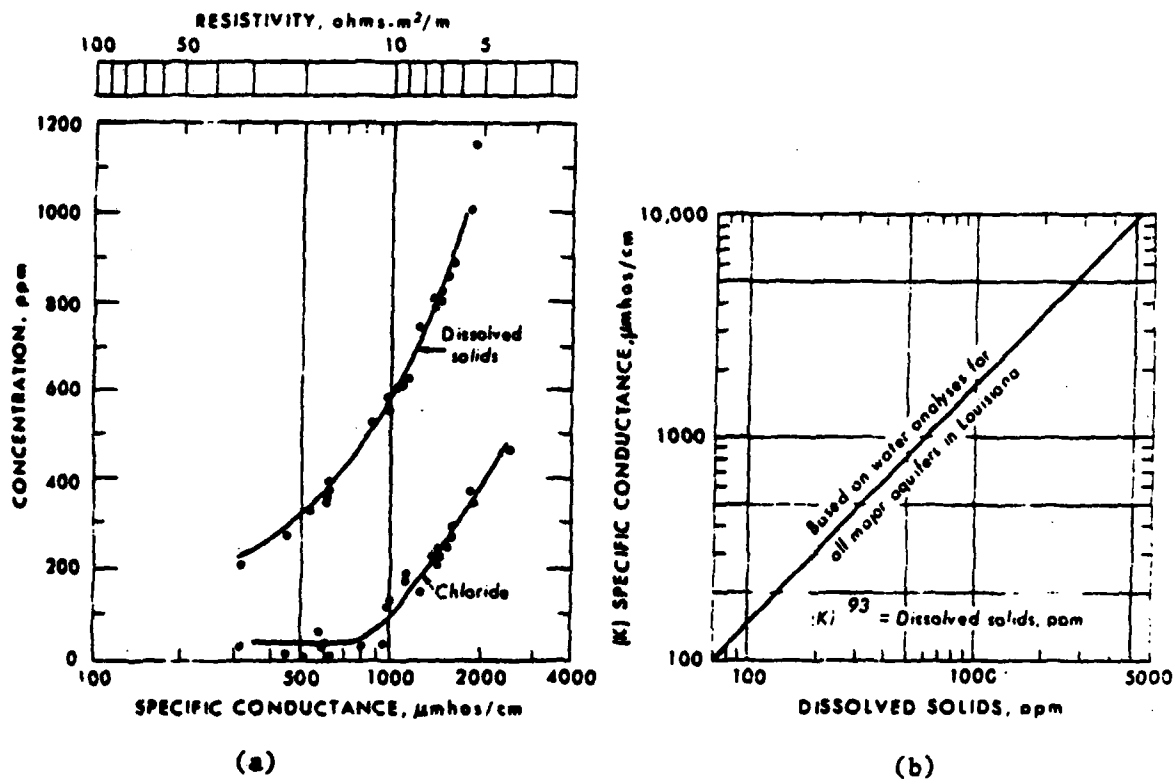


Figure 67. (a) Relation of Dissolved Solids and Chloride Concentration, in ppm, to Resistivity and Specific Conductance. (b) Relation between Specific Conductance and Dissolved Solids.

Source: Keys and MacCary, 1971.

amplitude of SP deflections across beds is related to electro-chemical and electrokinetic effects (ion migration). Electric logs are widely used for hydrologic applications (Table 21).

- (6) Thermal logging: can be used to detect flowpaths for groundwater and thermal anomalies due to exothermic chemical reactions in solution.
- (7) Tracer-tests: employ radioactive or neutron-activated chemical tracers to chart groundwater flowpaths and plume spreading characteristics between wells.
- (8) Sonic Televiewer (Teleseis): provides continuous sound images of the borehole wall to detect or verify discontinuities, porosity contrast, spacing and orientation of fractures and help to identify the depth intervals requiring in-situ testing.

Observation boreholes also permit integral sampling of cores extracted and the installation of borehole monitoring instrumentation (for seismic activity and water quality sampling, such as piezometers and stream gauges). Less commonly used logging techniques are:

- The Mise-a-la-masse (MLM) logging technique, which consists of simultaneous acquisition of both resistivity and induced polarization, has recently become widely used.
- The Thermal Decay Time (TDT) log records rate of decay of thermal neutrons (produced by a neutron source) in the borehole fluid and walls. It is a good indicator of salinity of formation water, since chlorine is a good neutron absorber. Porous hydrocarbon or gas-bearing zones and shaly formations can be resolved based on characteristic neutron-capture capability.

Recent advances in borehole logging instrumentation consist of complete logging units, which are light, portable, and controlled by microprocessors. For example, the Mount Sopris (Series III) system is compact, can be slung for helicopter transport, and records up to four channels of simultaneous logging data on a magnetic tape. Various sondes (spectral gamma-ray by Mt. Sopris, the magnetic susceptibility Kappalog sonde by OYO Instruments) and various electromagnetic sounders (Sirotem by Geox and EM-37 by Geonics) have been recently refined for borehole logging.

Geophysical field computers and calculator programs for geophysical application (listed and compiled by the Society of Exploration

Geophysicists) are available for rapid reduction and interpretation of field logging data. The Schlumberger (1979) log interpretation charts, as well as companion reference volumes on the Principles and Applications of Logging Techniques (1972, 1974), offer a useful field reference for rapid interpretation of crossed log charts.

4. MONITORING FIELD SAMPLING AND ANALYSIS METHODS OF GROUNDWATER INVESTIGATION

The following sections discuss various equipment and procedures that can be used to collect and analyze groundwater samples. This material is intended as a general overview of these topics and does not attempt to specifically define or recommend any procedure or technique. Generally, comprehensive sampling and analysis protocols can only be developed in response to a specific problem. Information presented in this section is intended to provide a background for decisions.

If specific information on sampling or analytical procedures is required, the reader is directed to the many references that exist in this area. A few specific references are presented throughout this section. Within the context of this discussion, the term "well" is meant to include both wells and piezometers.

a. Sampling Considerations

The objective of an environmental sampling operation is to collect a portion of some material (e.g., groundwater, wastewater, solid waste, etc.) and deliver it for analysis in a way that preserves the integrity of the sample. Preservation of integrity may require that the sample be unchanged (chemically, physically, or biologically) or it may allow for their controlled modification.

Obtaining a sample of groundwater from an aquifer or the vadose (unsaturated) zone above an aquifer being monitored may be done using a variety of sampling equipment and procedures. Different equipment/procedure combinations affect the sample. Thus, it is essential that all factors affecting the nature of the groundwater sample collected be considered before a sampling program is chosen.

Several types of sampling equipment are commonly used to collect samples from groundwater monitoring wells. These include devices that are as simple as a bucket and as complex as multistaged centrifugal pumps. Each of these have their own advantages and disadvantages (discussed later), and each may be used to fulfill the requirements of some particular program. Before any of these devices are applied to a particular program, however, their capabilities should be considered and reviewed with respect to the goals of the program and to factors that may influence how they should be used.

Several factors require consideration, including the depth of the water, the physical dimensions (e.g., overall well depth, length of the screened section, well casing diameter) and the rate at which water

flows into the well after initial volumes are removed. In the selection of sampling equipment, the materials of construction should also be considered, as this may affect the integrity of the sample. The residence time of water in a well is important because collection of water that has become trapped in a well casing may produce samples that do not reflect the character of the groundwater that currently exists in the geological formations that are being monitored.

Several of these factors depend on the hydrology/geology of the study area and as such they cannot be changed. However, sampling procedures can be developed which partially control the way in which they occur, making it possible to collect samples with various types of equipment. A few of these procedures are described below.

The water above the open or screened section of a well is considered to be stagnant with respect to the water that is in the screened section. This is true because the water in the screened section is constantly being replaced with water from the aquifer and, therefore, has had more recent exposure to geological formations outside of the well casing. Water contained above the open area is trapped, and changes in its composition may have occurred due to extended periods of exposure to well casing materials and the atmosphere. Therefore, the stagnant water is not necessarily representative of the surrounding groundwater. To obtain a representative sample from the well, stagnant water must be excluded. The sample should be drawn from below the fresh/stagnant water interface in a way that keeps the stagnant water from the sample.

Two different procedures may be used to limit undesirable mixing. The first approach, frequently used, requires the removal of a large volume of water before the sample is collected. Generally, a volume equivalent to 3 to 5 times the amount of water originally contained in the entire well is recommended (USEPA, 1980b). This procedure is based on the assumption that as first-time water is removed, most of the stagnant water is displaced by fresh water from the aquifer. Removal of additional water is designed to flush the well casing, rinsing away any residual contaminants. Even if all of the stagnant water is not removed the first time the well is prebailed, the removal of five volumes of water will greatly reduce the amount that is contained in the sample. For example, if we assume that 100 percent of the well water is stagnant and that only 50 percent of the water originally contained in the well may be removed each time the well is bailed, then 5 prebailing repetitions will provide a final fresh/stagnant mixture that is roughly 97-percent fresh and 3-percent stagnant. If 33 percent of the initial well water is removed per volume bailed, then by the fifth prebailing repetition the fresh/stagnant mixture remaining is 87-percent fresh and 13-percent stagnant. Additional prebailings are recommended to further reduce the stagnant water content of the well.

A second approach is to selectively remove water from different levels of the well. Using this approach, one well volume of water is removed from the well from a location as high above the fresh/stagnant

water interface as is possible. The fresh/stagnant water interface is assumed to coincide with the upper elevation of the open (screened) section. The point from which the initial well volume is removed is determined by the individual characteristics of each well; this includes factors such as well depth, groundwater depth, and the rate of well recharge. If the well does not recharge as quickly as water is being removed, it may be appropriate to evacuate the stagnant water by locating the sampling point at or just below the fresh/stagnant water interface. Once the stagnant water is removed, the sampling location would be dropped to a point near the bottom of the screened section prior to sample collection.

The application of this procedure either completely removes the stagnant water or keeps it at a point high enough above the final sampling point to prevent undesirable mixing. This multilevel pumping approach also requires the removal of considerably less total water volume, thereby allowing each well to be sampled in less time than the approach that requires the removal of 3 - 5 well volumes. If properly performed, it will deliver a sample representative of the surrounding aquifer.

Another factor to be considered before a well is sampled relates to whether there are advantages to measuring some chemical parameters in the field as the water is removed. Determinations of chemical parameters, such as pH, conductivity, dissolved oxygen (DO) content, oxidation-reduction potential, water temperature, and a few specific ion (Cl^- , CN^-) concentrations, can easily be made in the field while the well is being prepared for sampling and after collection of the sample. Parameter measurement is not always appropriate during sample collection because some of these techniques (pH, DO, etc.) use electrodes that release small quantities of chemicals into the water. However, determination of these parameters immediately before and just after the sample is collected does provide some information on the homogeneity of the water being removed from the well. For example, if two readings of parameters that are separated by some predetermined volume of water (e.g., one screen volume) prove to be equivalent, the water may have reached some momentary level of equilibrium and a sample may then be taken to represent that condition. If a set of readings taken subsequent to sample collection shows equivalent values, then it may be inferred that the water obtained is representative of the volume that has been bracketed. If the readings are different, then provisions can be made immediately to establish a new level of equilibrium within the well and to collect a new sample.

Groundwater parameters can be measured regardless of the type of sampling equipment used. If a noncontinuous supply of water is available, parameters may be measured by placing aliquots of the recovered well water into beakers, followed by the determination desired. In systems where continuous sample streams are available, the electrode or probe assemblies of many meters can be mounted directly into a flow through cell and the parameters continuously monitored.

In programs concerned with organic species pollution, field extraction of organics is a convenient method of preparing the sample for analysis, while decreasing the possibility of sample degradation during shipment. Different systems can be set up for inline extraction of organics with equipment that provides constant flows of water from the well (Figure 68). With sampling equipment such as bailers, an additional pump must be used to channel the sampled water through the sorbent cartridges.

There are five general categories of groundwater monitoring equipment and one type of equipment normally used for vadose sampling. These include:

- Manual collection equipment
- Vacuum extraction equipment
- Pneumatic or pressurized collection equipment
- Mechanical collection equipment
- Gas entrainment equipment
- Lysimeters (vadose zone)

Each of these types of equipment will be more completely discussed in the following sections. During the review of each of these sections, the reader should keep in mind that it is essential to be able to control where and how the water is drawn from a well to insure that it is as unaffected by the combined sampling process (well installation and sample collection) as possible.

b. Manual Sampling Equipment

Manual groundwater sampling equipment includes all devices that require or involve the use of repetitive manual manipulation. Generally, these devices may be grouped into two classes, one including bailers, and the other devices such as hand or foot pressure/vacuum pumps. Examples of these types of equipment are shown in Figures 69 to 72.

Both of these alternatives involve simple equipment, and are generally easy and inexpensive to implement. A major disadvantage in their use is that their operation is tedious and time consuming. If a specific monitoring location is expected to be sampled frequently, alternative sampling procedures and permanent installations may be more suitable.

Manual bailing is straightforward and basically equivalent for any of the bailers shown in Figures 69 to 71. Procedurally, the bailer is repeatedly lowered into the well, allowed to fill with water, raised to grade surface, and emptied until the required sample volume has been removed. Bailers that load from the top (Figure 69) or from the bottom (Figure 69) are common.

One disadvantage of top-loading bailers is that they cannot be used to evacuate a well to dryness. Another potential drawback of top-

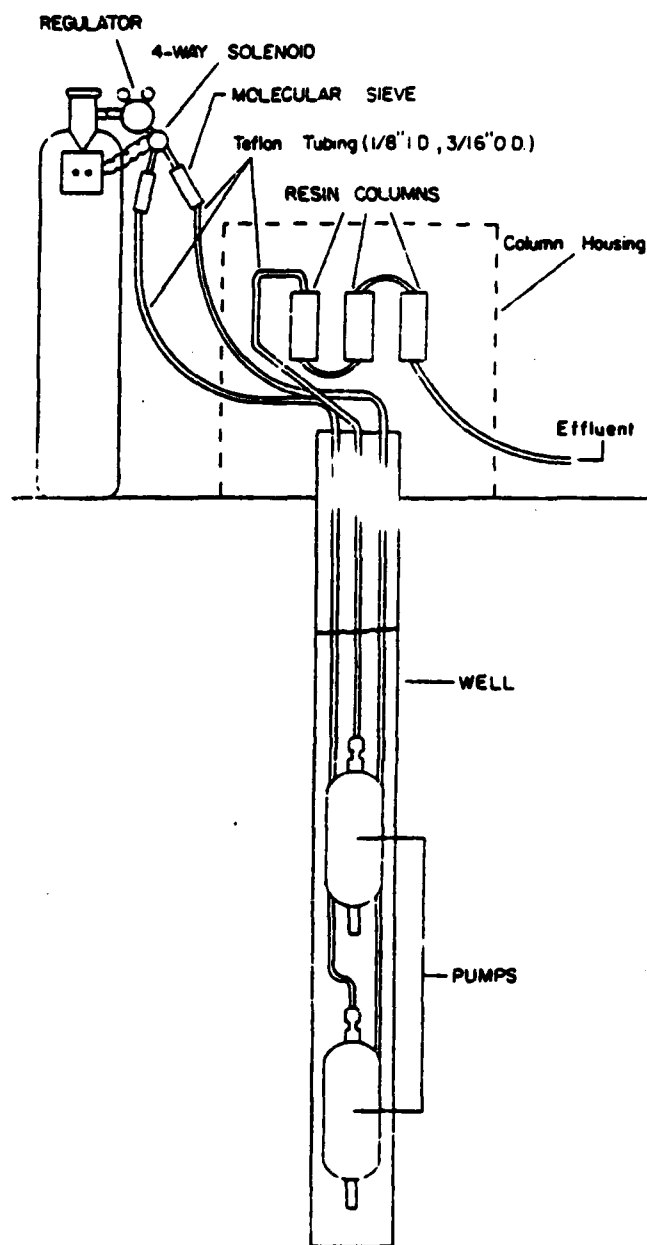


Figure 68. Example of an Organic Extraction System

Source: Pettyjohn, W.A. et al., "Sampling Groundwater for Organic Contaminants," Ground Water, Volume 19, Number 2, pp. 180-189, © March-April 1981.

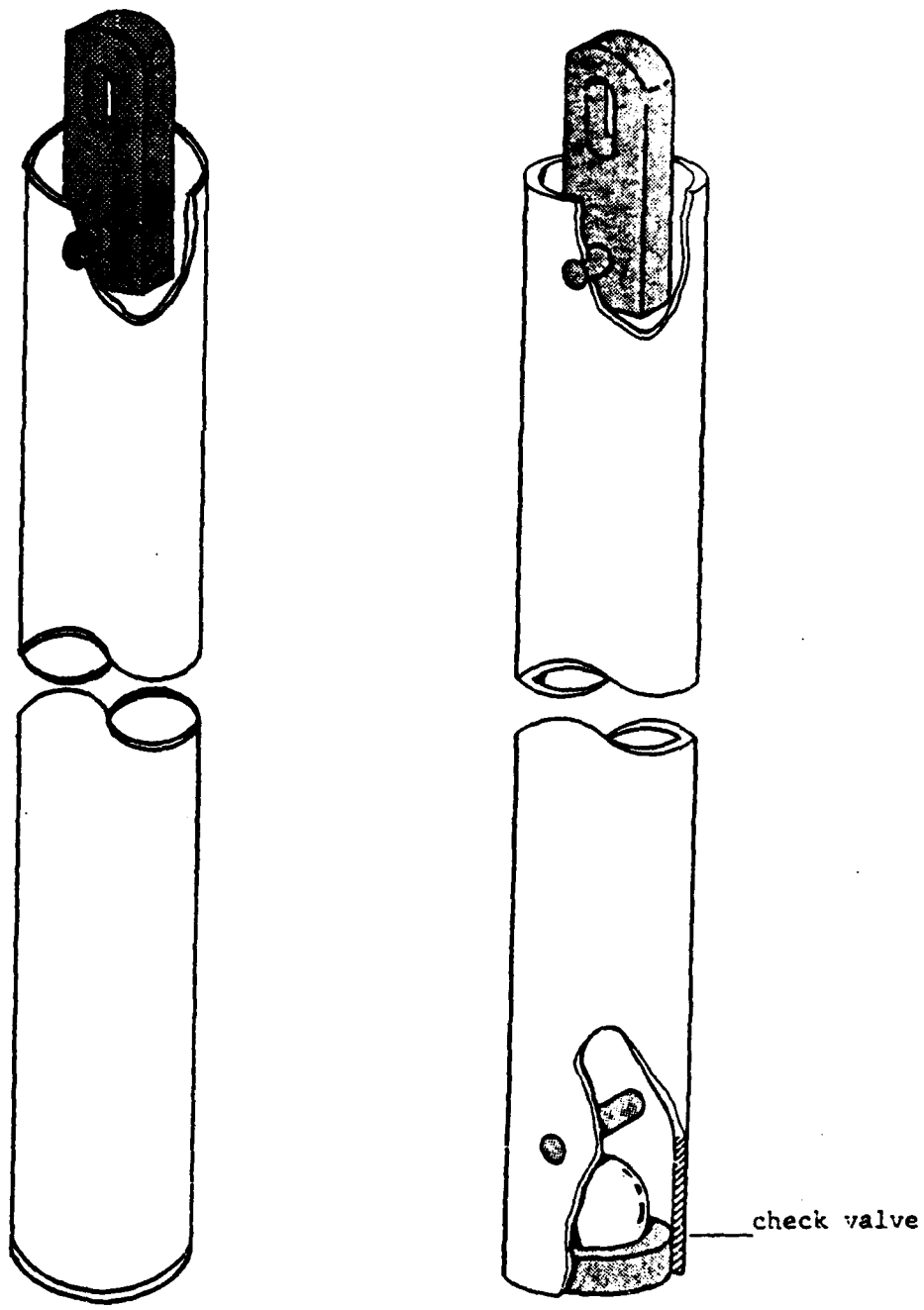


Figure 69. Top-loading and Bottom-Loading Bailer

Source: Timco Mfg.

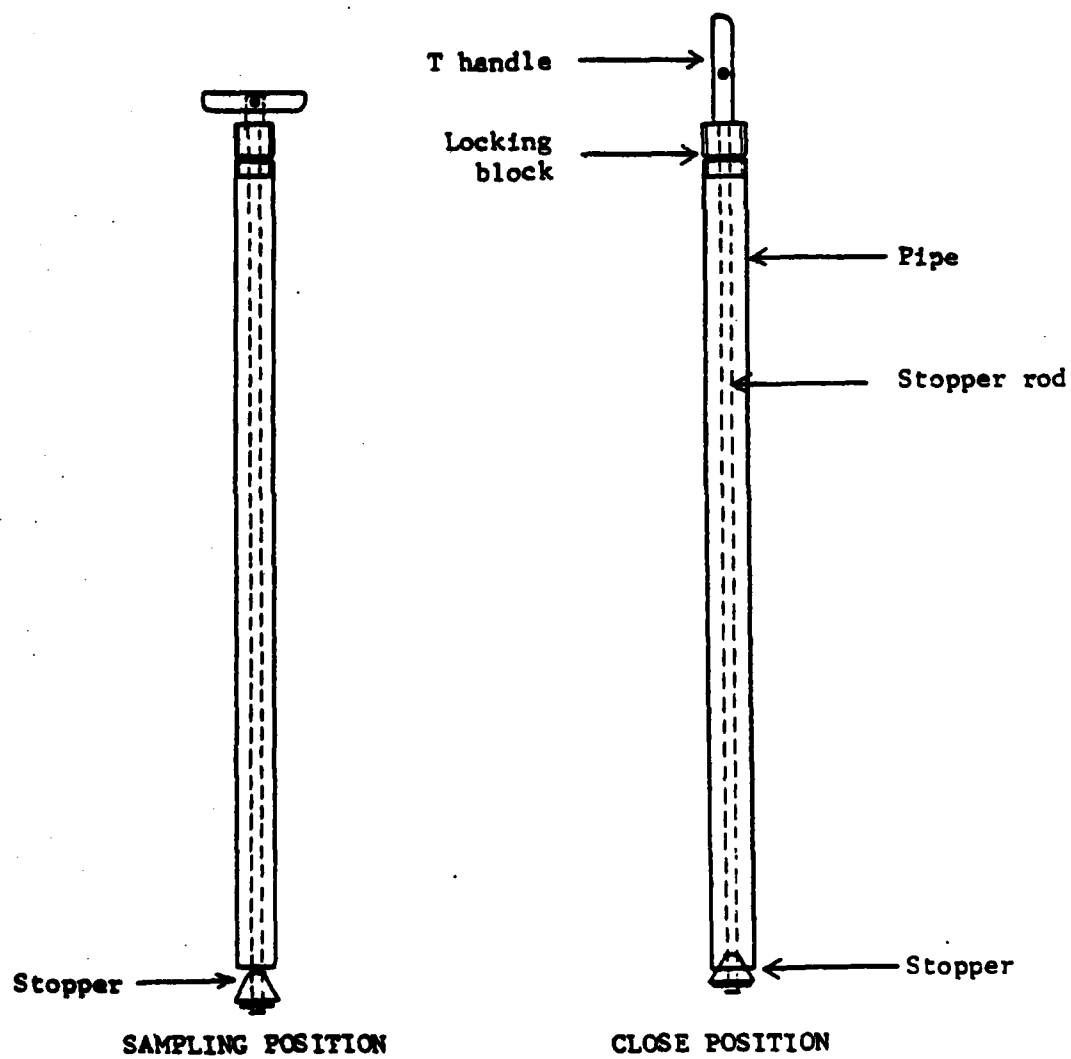


Figure 70, Coliwassa Sampler.

Source: EPA, 1980b.

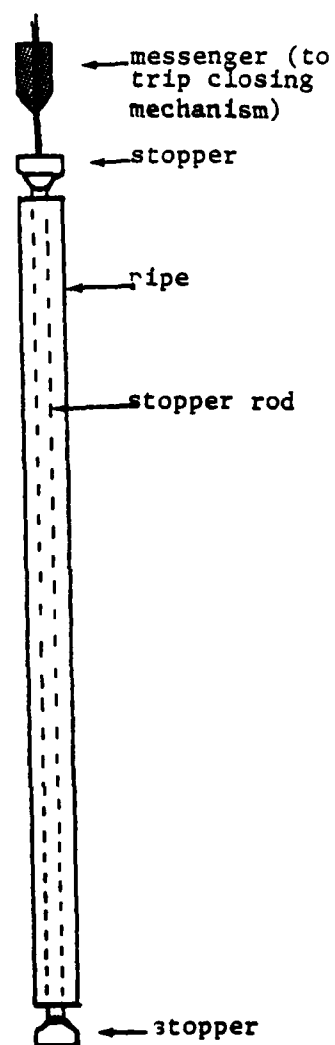


Figure 71. Kemmerer sampler. (Flow through).

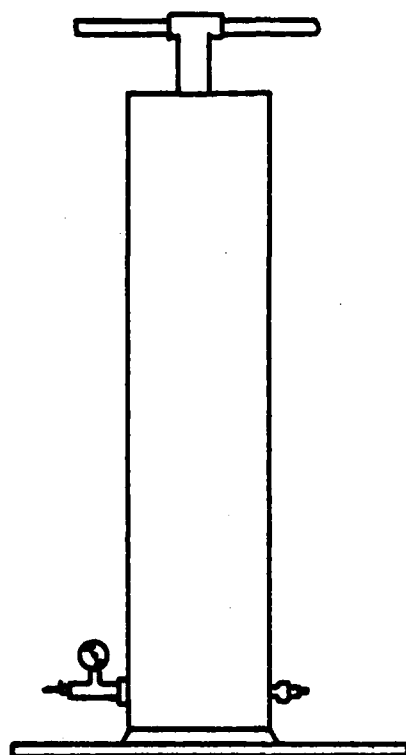


Figure 72. Pressure-vacuum Hand Pump.

loading bailers is that they may be buoyant and difficult to fill if improperly constructed.

Bottom-loading bailers can recover more water from a well, and they will not be buoyant. Kemmerer and Coliwassa bailer designs, such as those shown in Figures 70 to 71, have the advantage in that they may obtain water from specified depths. When the Coliwassa bailer is used, the closed bailer is lowered to the desired horizon before it is opened. Once opened, water from that horizon enters and the bailer is then closed and raised. The Kemmerer bailer, on the other hand, is lowered into the well with both ends opened, allowing water to flow through it. Once the desired depth is reached, the sampler is closed and it is raised to the grade surface. One major disadvantage of all bailers is that the water column contained in the well is subjected to considerable mixing during sampling. Stagnant and fresh water may combine; offgasing of volatile species may occur; or air may be introduced into the water. All of these disturbances may result in chemical changes in the water being sampled. Additionally, unless considerable care is exercised in handling the attached rope during sampling, large quantities of soil, pebbles, grass, etc., may be introduced into the well. Despite the many obvious drawbacks of the manual bailer, it is one of the most common methods of groundwater sampling.

Hand-pumping techniques are also time consuming and tedious. However, these techniques are better than manual bailer approaches because more control of water sample origin may be achieved by the use of various sample collection installations. One drawback of these devices is that suction lift and pressure capacities are somewhat limited. Generally, only 4.5 meters (15 feet) of suction lift is attainable, and pressure limits are on the order of 42 kg/cm² (60 lbs/in²). Higher vacuum/pressure limits may be obtained, but this is usually done at the expense of sample volume throughput.

c. Vacuum Collection Equipment

Vacuum pumps powered by gas or electric motors are a very convenient and efficient means of obtaining groundwater samples. The objective of this type of design is to produce a vacuum on some type of well installation (usually inert sampling lines), and draw water to the surface by means of a pressure differential. Peristaltic and diaphragm type pumps (supplied by Horizon/Ecology, Cole Parkman Instrument Corporation, or Fisher Scientific) can be hooked up to the inert sampling lines and can rapidly evacuate the desired volume of water. The major advantage of this type of well sampling is that water can be easily removed from different depths. Small volumes of water can be removed while still insuring that the well has been flushed properly, and reducing the sampling time. This equipment provides a constant supply of water from the well to the surface, helping in the logistics of the above ground sampling process.

A disadvantage of vacuum pump sampling collection is that there is a limit as to how far the pump is capable of lifting the water from

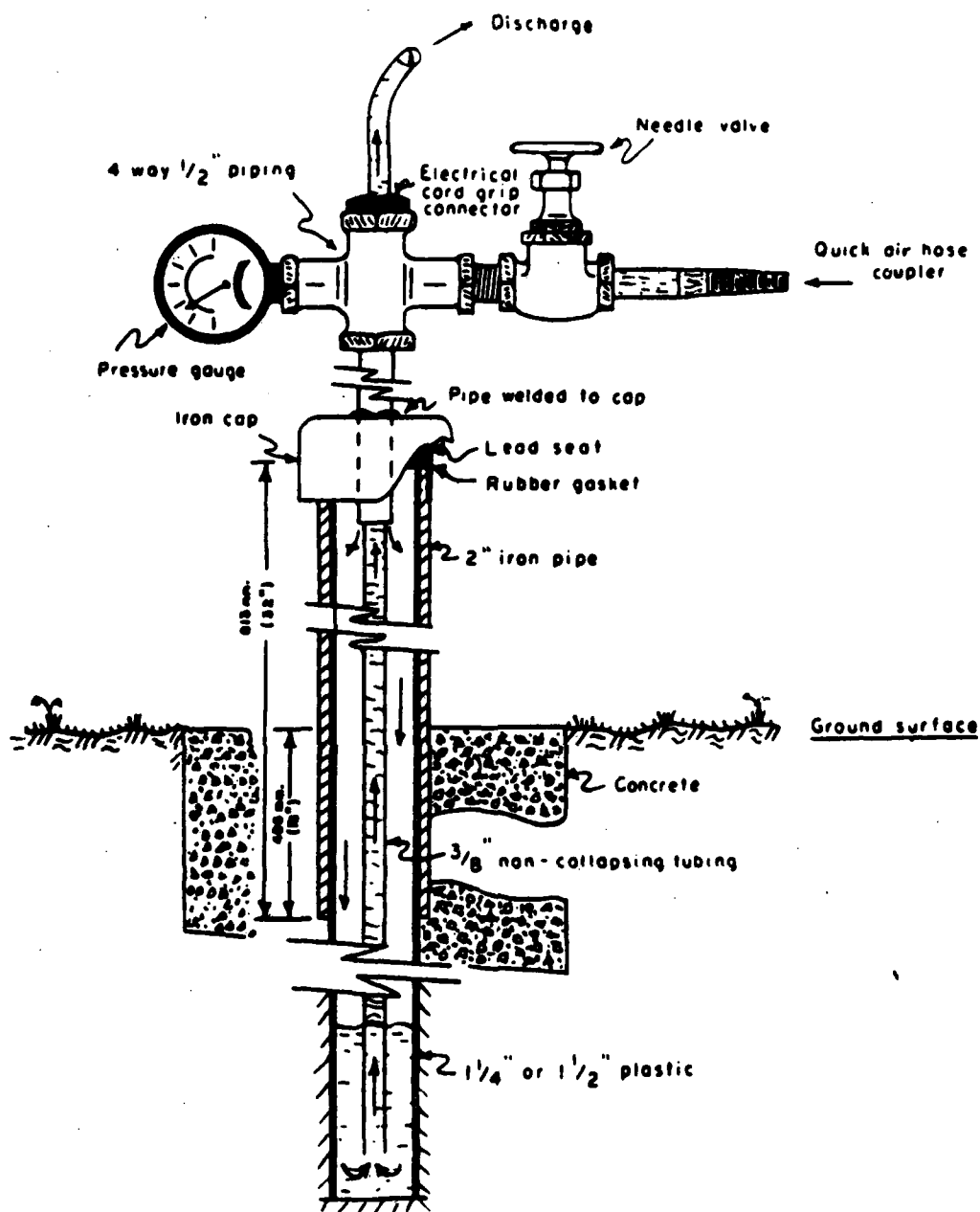


Figure 73. Well Casing Used as Pneumatic Collection Vessel

Source: Sommerfeldt and Campbell, 1975.

the well (approximately 25 - 30 feet). For groundwater depths in excess of this level, multistage vacuum systems would have to be used. These systems are expensive and require extensive site preparation.

A second major disadvantage of vacuum sampling systems is that by applying a vacuum, the volatile species dissolved in the water may be driven out of solution, therefore, changing the chemical composition of the water being sampled. This is of particular concern when sampling for organic species.

d. Pneumatic or Pressurized Collection Equipment

Pneumatic pressure can be used very effectively to collect groundwater samples. Pressure can be used to pump wells through many various designs of equipment, but they all work on the same principle. Water contained in some sealed area in the well is forced by gas pressure up to the ground surface through a sampling line (Figure 73). Two lines extend to the sampling device; one stops just below the seal and the other extends to the bottom of the sealed area. Pressure is exerted on the water from the shorter line, and the water is forced up the longer line to the surface.

Pneumatic pressure can be applied by manual powered pumps, but as has been previously discussed, these devices generally have pressure limitations. Electric and gasoline-powered engines or bottled gas can provide pressure up to 175 kg/cm^2 (250 lbs/in^2). Pressures of this level are adequate for pumping wells of depths up to 100 meters (320 feet).

The simplest pneumatic device uses the well casing as the collection vessel. A well cap is used to seal the well, and two lines are introduced through the cap. One line extends to the point near the bottom of the well, while the second stops just below the cap. An example of this installation is shown in Figure 73. The shorter sampling line is used to pressurize the well, while the longer channels water to the surface. While this approach will deliver a water sample to the surface, it is not recommended because it will also cause water contained in the well to backflush into the aquifer, thereby minimizing recovered volumes. Furthermore, if the well is improperly pressurized, the compressed gas may be forced into the aquifer and be trapped outside the well casing. This may cause changes in the flow patterns around the well.

To prevent these problems, a separate collection vessel (i.e., pump) can be placed in the well and used to control movement of pneumatic fluid and water. Many existing pump designs have been used (Figures 73, 74, and 75). Although there are some differences in configuration, they all operate on the same principle. These pumps have many advantages; they can sample water from very deep wells; they can pump water rapidly as compared to the previously discussed bailer and vacuum methods; and they may provide a reasonably steady stream. It is also possible to raise and lower the pump within the well during

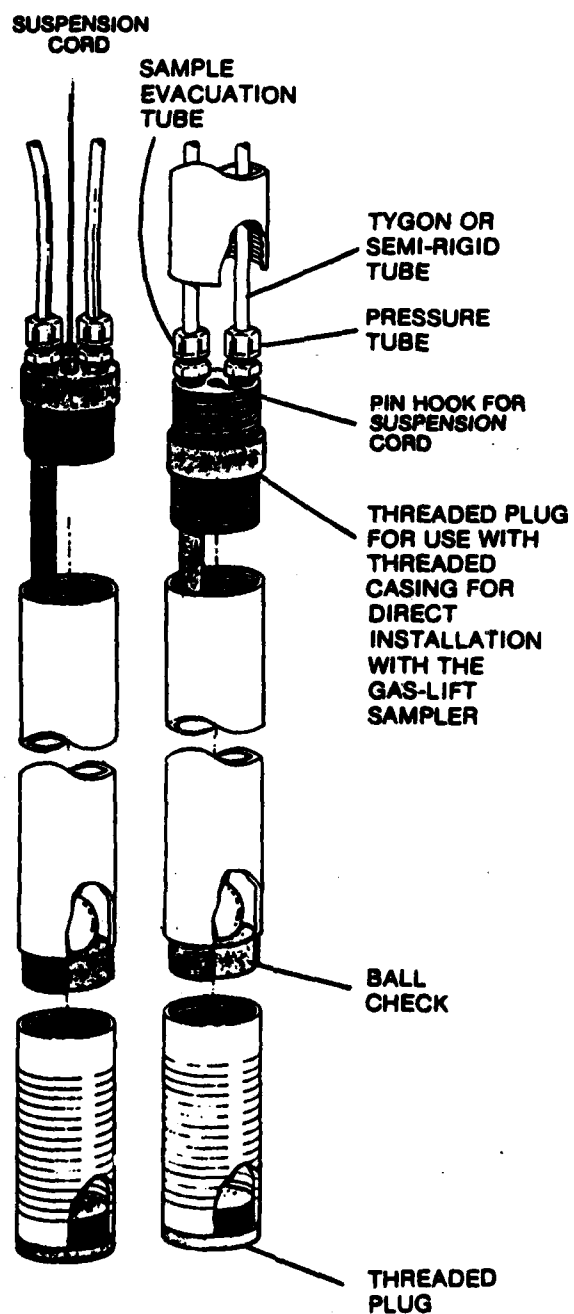


Figure 74. Basic Pneumatic Pump

Source: Timco Mfg. Co., Inc.

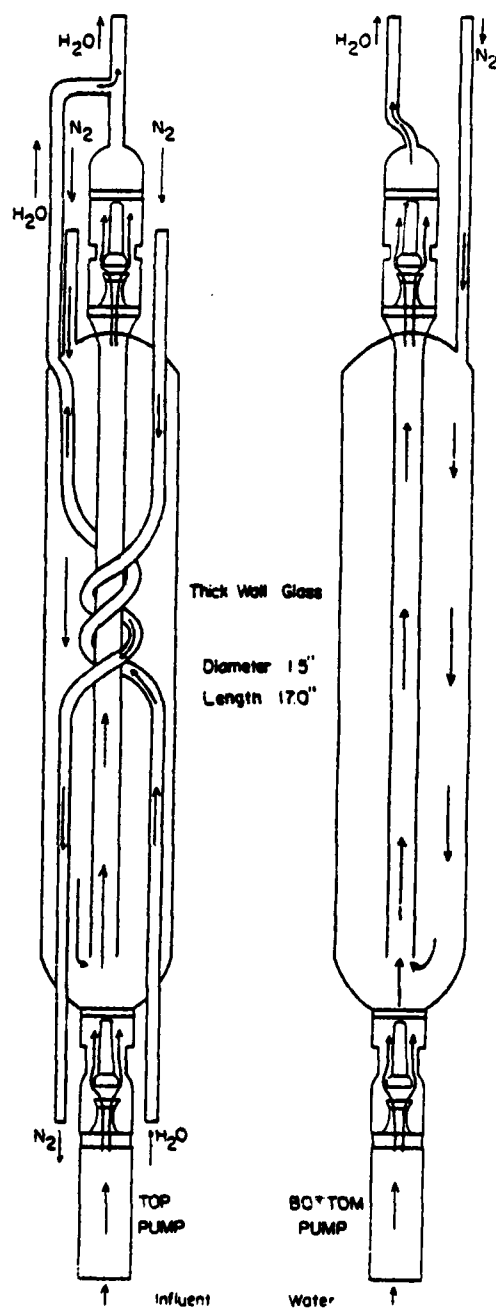


Figure. Continuous Discharge Pneumatic Pump

Source: Pettyjohn, W.A. et al., "Sampling Groundwater for Organic Contaminants," Ground Water, Volume 19, Number 2, pp. 180-189, © March-April 1981.

sampling, thereby allowing for water to be obtained from specific levels within the well. This movement of the pump in the well induces a considerable amount of mixing of the water column; however, if the sampling procedure is designed properly, this should not present a problem as all the stagnant water originally contained in the well should be removed or positioned well above the sampling point before the sample is taken.

The major drawback to this type of sampling equipment is the constant exposure of the groundwater to the pneumatic fluid being used to drive the pump. Some designs eliminate the constant exposure of the water and the pneumatic fluid, such as piston type and bladder type (Figure 76) pumps. These designs are very expensive and difficult to construct. Many different sources of pressurized gas are in use: automobile engines (Trescott and Pinder, 1970), gas and electric compressors (Summerfeld and Rampbell, 1975), and bottled gas (Tomson et al., 1980). An understanding of the analysis to be done on the water samples is necessary to assess the benefits and disadvantages of each pneumatic fluid option. Using an inert gas such as purified nitrogen does not eliminate the possibility of chemical alteration of the sample, but reduces it to a minimum. Automobile engines and gas compressors do supply adequate pressures, however they may introduce impure and reactive gases which can affect the chemical composition of the water being sampled.

e. Mechanical Pumping Systems

Groundwater samples may also be obtained by the use of any of a number of types of mechanical pumps. Within the context of this discussion, mechanical pumps include all submersible pumps that are driven by electric or gasoline-powered motors. Classic examples of this type of pump include reciprocating or piston pumps and centrifugal pumps. Reciprocating pumps move water by alternately compressing and decompressing a trapped volume of water confined in a fixed diameter barrel.

In their simplest form, reciprocating pumps consist of a single barrel or cylinder divided into two sections by the plunger. The lower section of this pump contains air that is isolated from both the well and the upper section of the barrel. The plunger is mechanically forced downwards, compressing the air and creating a partial vacuum in the upper chamber. Water from the well enters and fills this chamber through a check valve assembly. The direction of travel of the plunger is then reversed, causing the water to be compressed. Since the inlet check valve prohibits the water from flowing back into the well, it is forced upwards into the supplied discharge line. A check valve may be placed on the discharge line to keep discharged water from reentering the pump. By continually alternating the path of travel of the plunger, well water is repeatedly drawn into and expelled from the pump, forcing it to rise to ground surface. By including additional plumbing and modifying the design, these pumping systems can be made to move water on

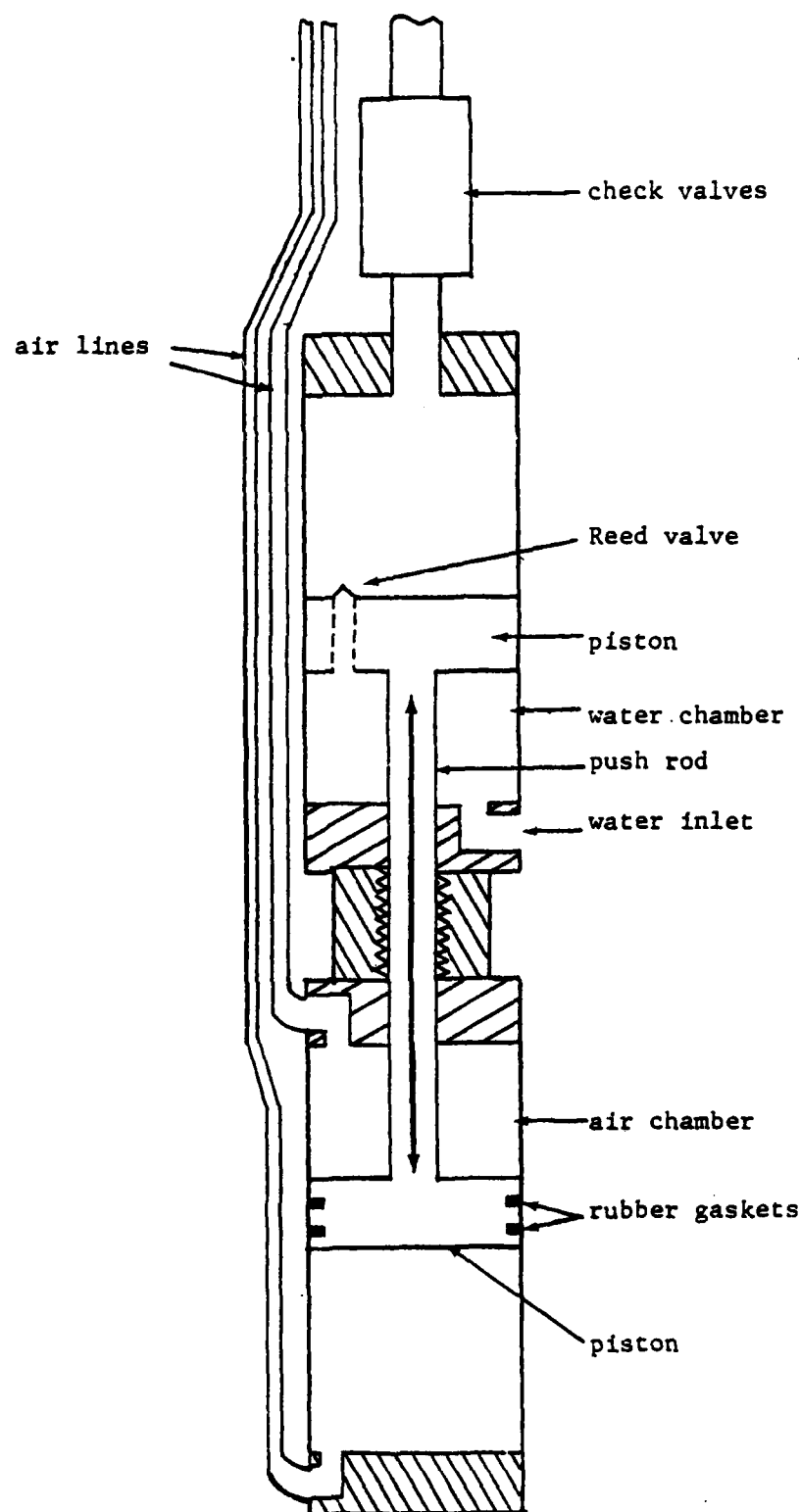


Figure 76. Piston Pneumatic Pump. (Notice Pneumatic Fluid does not Contact Water During Operation).

Source: Hillerich, 1977.

both the up and downward stroke, providing a more continuous supply of water to the surface.

Centrifugal pumps force water out of a well by imparting a spinning motion to small, sequential volumes. The principal component of this type of pump is the pump head which contains an impeller. Water from the well enters the pump head through an inlet provided near the center of the pump head. When the impeller is set spinning, water contained in the pump head is thrown outward towards the outer edge of the pump head housing, causing a slight vacuum to be created in the center. This vacuum is immediately filled by water from the well. Water initially thrown outward is now at a slightly higher pressure than other water contained in the pump head, and it is forced through a discharge line to the ground surface. As the impeller continues to spin, more and more water is drawn into and spun out of the pump head, forcing a column of water to the ground surface. By mounting multiple-impeller assemblies atop each other, considerable water pressure can be exerted on the water, allowing for very deep wells to be sampled.

Designs of centrifugal and reciprocating pumps that use either compressed gas streams or manual manipulations to power the impeller or piston are available. These devices are considered in other sections of this document.

A major advantage of mechanical pumps is that they do not require much attention or manipulation after they are initially installed. Once in place, they can deliver large quantities of water at a steady pressure and a constant flow rate. Another advantage of this type of system is that the chemical, physical, and biological integrity of the sample is maintained because no external gases are introduced or mixed with the sampler. Furthermore, while high flow rates are obtainable, mixing and turbulence of the water stream is not violent.

A principal disadvantage of this sampling alternative is that pumps of this nature are generally large and usually cannot be used in wells smaller than 3-4 inches in diameter. A second disadvantage of these systems is that a power source may not be available at all sampling locations.

f. Gas Entrainment Systems

Gas entrainment or air lifting represents another approach that may be used to obtain groundwater samples from a well. This technique is similar to the pneumatic systems previously described; except in this case, the gas is allowed to bubble through the groundwater rather than being controlled. An example of a typical gas entrainment sampling system is shown in Figure 77.

Gas entrainment systems require two sampling lines to be installed in a well. One of these lines is larger in diameter than the other, and both extend from the ground surface to a point that is below the groundwater surface. The larger of the two lines is used to channel the

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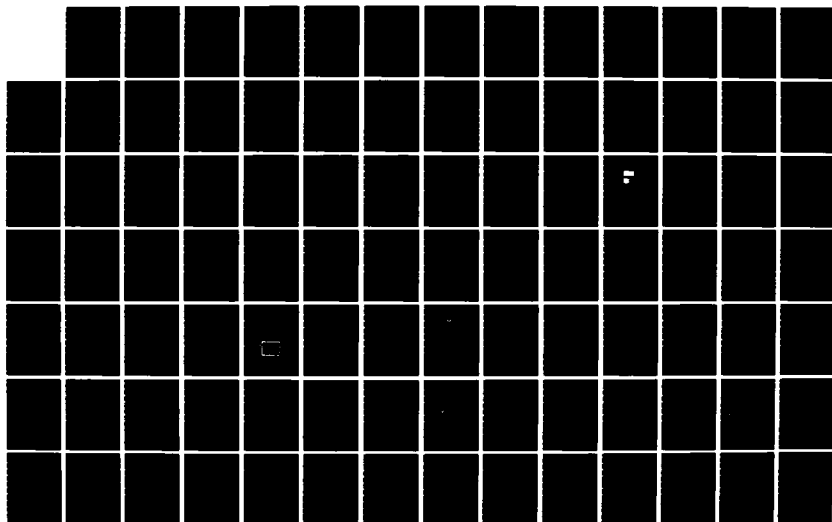
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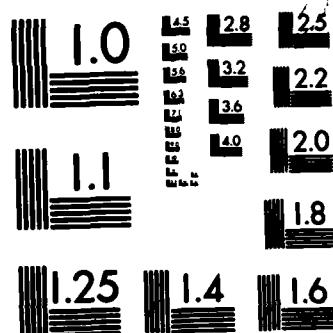
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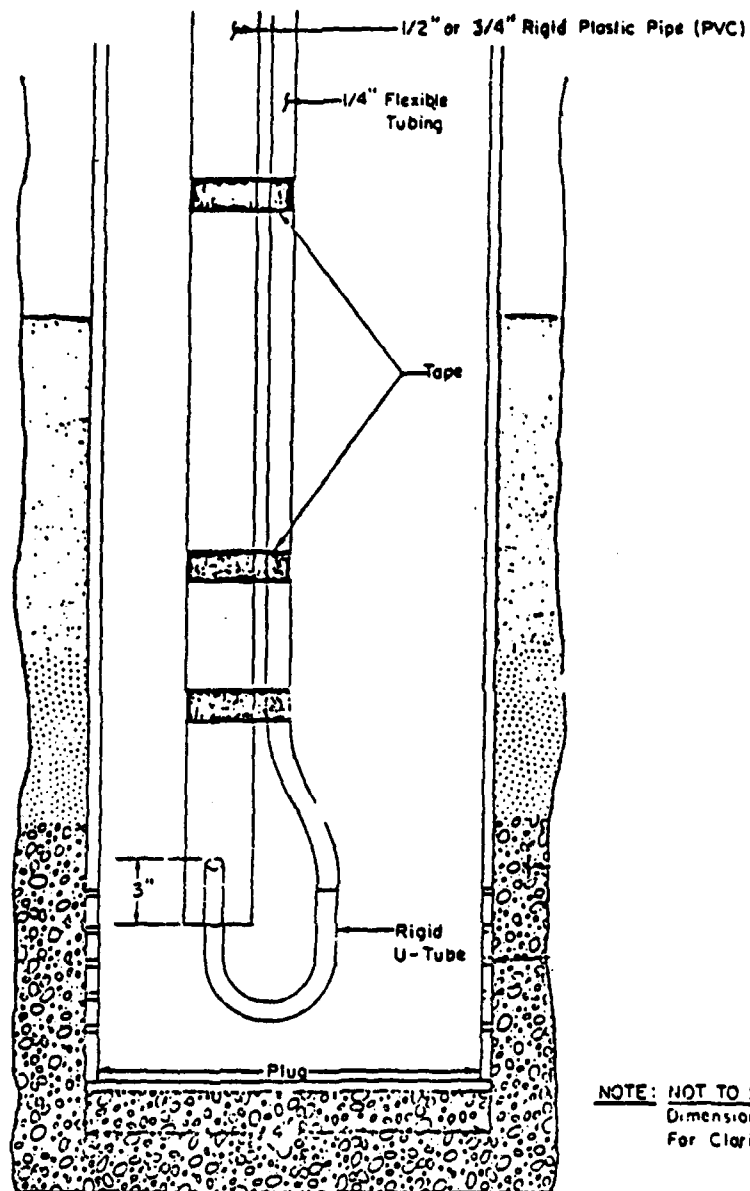
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NOTE: NOT TO SCALE
Dimensions Exaggerated
For Clarity

Figure 77. Gas Entrainment Pumping System
Source: Ginilka and Harwood, 1979

sample water/gas mixture to the ground's surface, and it is generally open to the atmosphere. The smaller of the two lines is used to channel compressed gas down into the well to a point inside the larger pipe where it is released. Once released, the compressed gas expands, forming a bubble whose size is limited by the inner walls of the larger tube. The density difference that exists between the gas bubble and the surrounding water causes the gas to rise and forces the water trapped above it to rise at the same time.

At land surface, the compressed gas/water mixture is directed to a point away from the well where the gas is allowed to escape and the water is collected. Compressed gas requirements for this sampling approach may be fulfilled using either bottled gases or with gasoline or electric-powered compressors. Of these sources, bottled gases are generally preferred because a more inert gas can be supplied for pumping.

Gas entrainment sampling systems have numerous disadvantages and are generally not recommended for studies which require precision analyses. The principal disadvantage of these systems is that the violent or turbulent mixing of the compressed gas with the sample water may alter chemical, physical, and biological integrity of the sample.

Another disadvantage of these systems is that they are inefficient. Generally, less than half of the groundwater present in a well can be recovered, meaning that more time must be spent in developing the well prior to sample collection.

g. Vadose (Unsaturated) Zone Sampling Systems

The vadose (unsaturated) zone, is sampled using devices called lysimeters. There are two basic versions of this device, one that uses both pressure and vacuum to deliver a sample, and a second type which uses only vacuum. Examples of these two lysimeters are shown in Figures 78 and 79.

In operation, a vacuum is drawn on the porous cup assembly which induces water to flow into the cup. Water collects in the cup and is sampled in one or two ways. Using the pressure-vacuum lysimeter, the cup is pressurized, forcing the water up through a sample collection tube. This procedure is identical to that described in an earlier discussion on the pneumatic sampling system.

The vacuum system uses a vacuum source to draw the water contained in the cup up to the ground surface. This technique option suffers the same suction lift limitations as the vacuum pumping systems previously discussed. Both techniques may lose volatile organics during sample collection.

A specialized lysimeter design has been developed by personnel at the Robert S. Kerr Environmental Research Laboratory at the U.S.

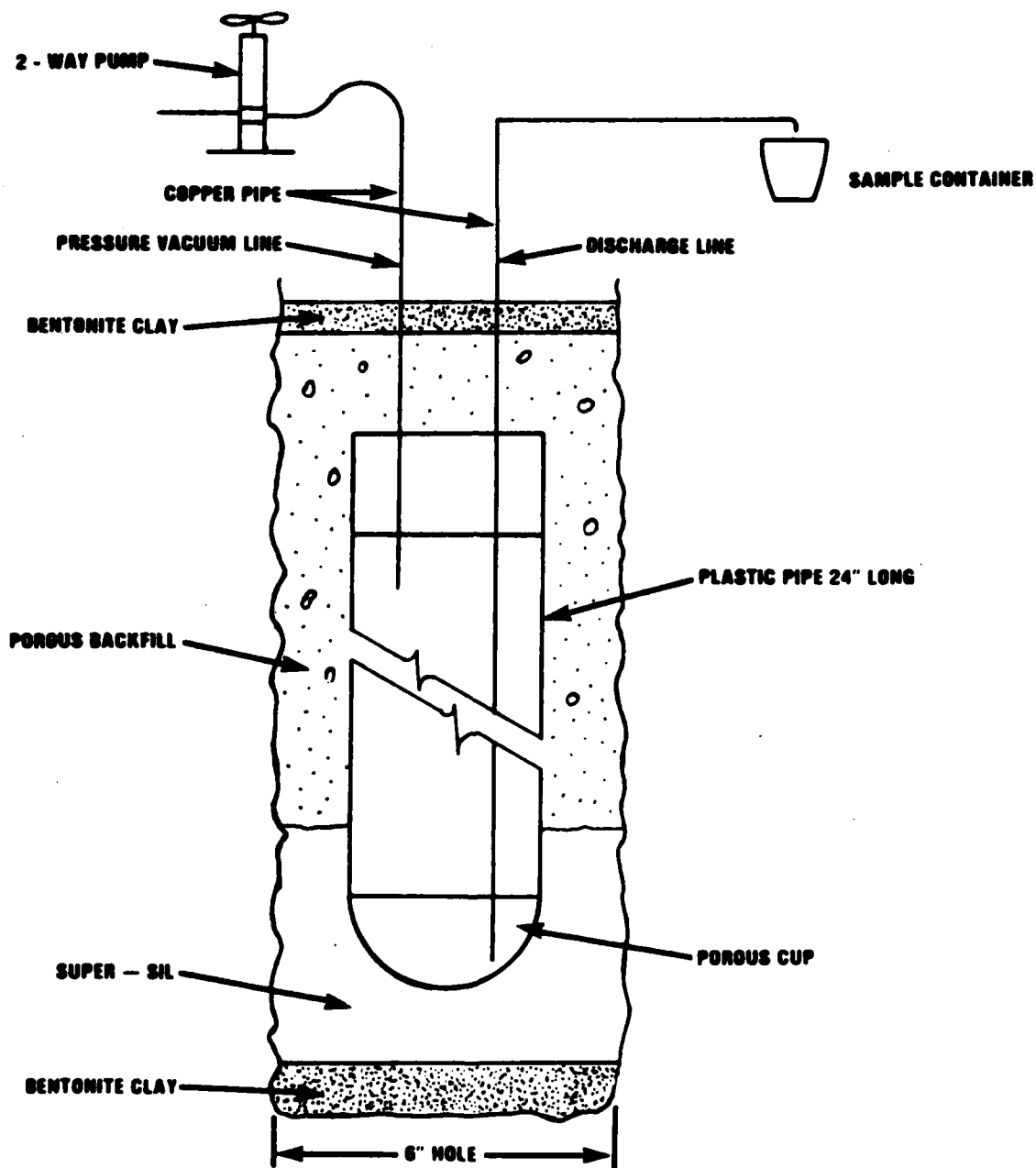


Figure 78. Example of a Pressure - Vacuum Lysimeter Installation
 Adapted From: Parizek, R.R. and B. E. Lane, "Soil-Water Sampling Using
 Pan and Deep Pressure-Vacuum Lysimeters," Journal of
 Hydrology, Volume II, pp. 1-21, © 1970.

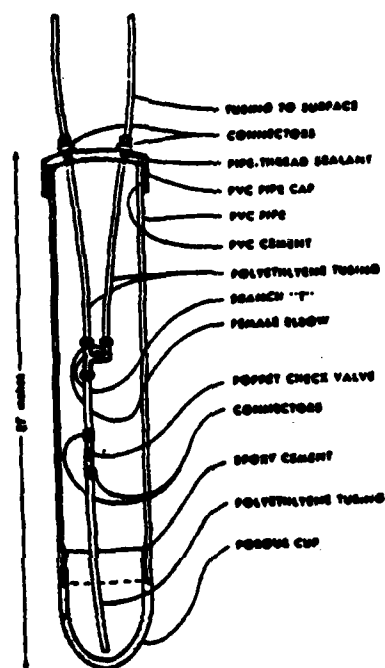


Figure 79. Vacuum-Vacuum Lysimeter Installation

Source: Wood, 1973.

Environmental Protection Agency. This system combines a pressure vacuum lysimeter with a purge and trap apparatus and is intended to provide a means by which volatile organic species may be collected and concentrated in the field. A diagram of this unit is shown in Figure 80.

h. Chemical Analysis

The analysis of groundwater samples, like the analysis of any material, may involve the utilization of equipment and techniques that span the entire spectrum of analytical chemistry. Particular problems encountered may be resolved simply, using nonsophisticated equipment and procedures such as pH meters or gravimetric determinations, while other problems encountered may require complex separation or fractionation techniques and sophisticated equipment such as gas chromatography/mass spectrometry. Thus, a comprehensive description of all procedures, protocols, and instrumentation that may be applied, is, by necessity, complex and beyond the scope of this manual. If specific information is sought, the reader is referred to one of the many references which describe analytical procedures.

The following discussion sections address various important aspects of the analysis portion of a program, including: sample preparation considerations, general analytical techniques, qualitative techniques which may be utilized in exploratory or screening phases, and the quantitative analyses.

1. Sample Preparation

The handling of a sample after collection and before analysis is, in most cases, defined by the specific analytical protocols being used. These are related to the nature of the sample being analyzed, as well as to the type of information needed. An example of a formal rationale for application of a set of analytical techniques is given in Figure 81. This protocol was designed specifically for characterization of water soluble, nonvolatile organic species in an aqueous stream.

In general, such protocols should address four important aspects of sample integrity:

- Protection of Sample Components - Losses of individual compounds of volatilization, adsorption or chemical reaction must be guarded against. Appropriate sampling containers, chemical preservation, and refrigeration will prevent the degradation/modification of the samples.
- Extraction of Components - Most methods used for the analysis of complex mixtures require that the organic components be extracted into an organic solvent. Ultimate selection of an appropriate solvent should address solvent efficiency and

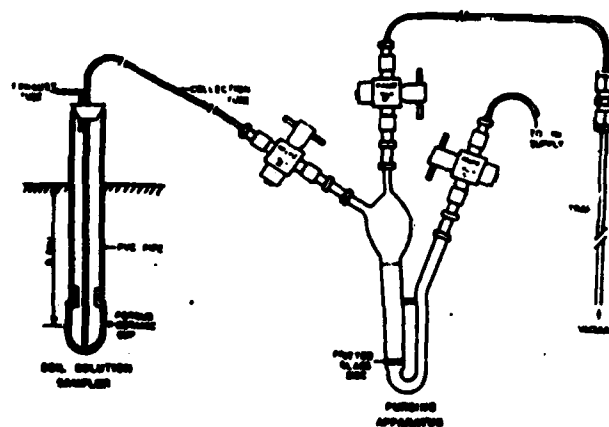


Figure 80. Lysimeter with Purge and Trap Setup

Source: Pettyjohn, et al., 1981.

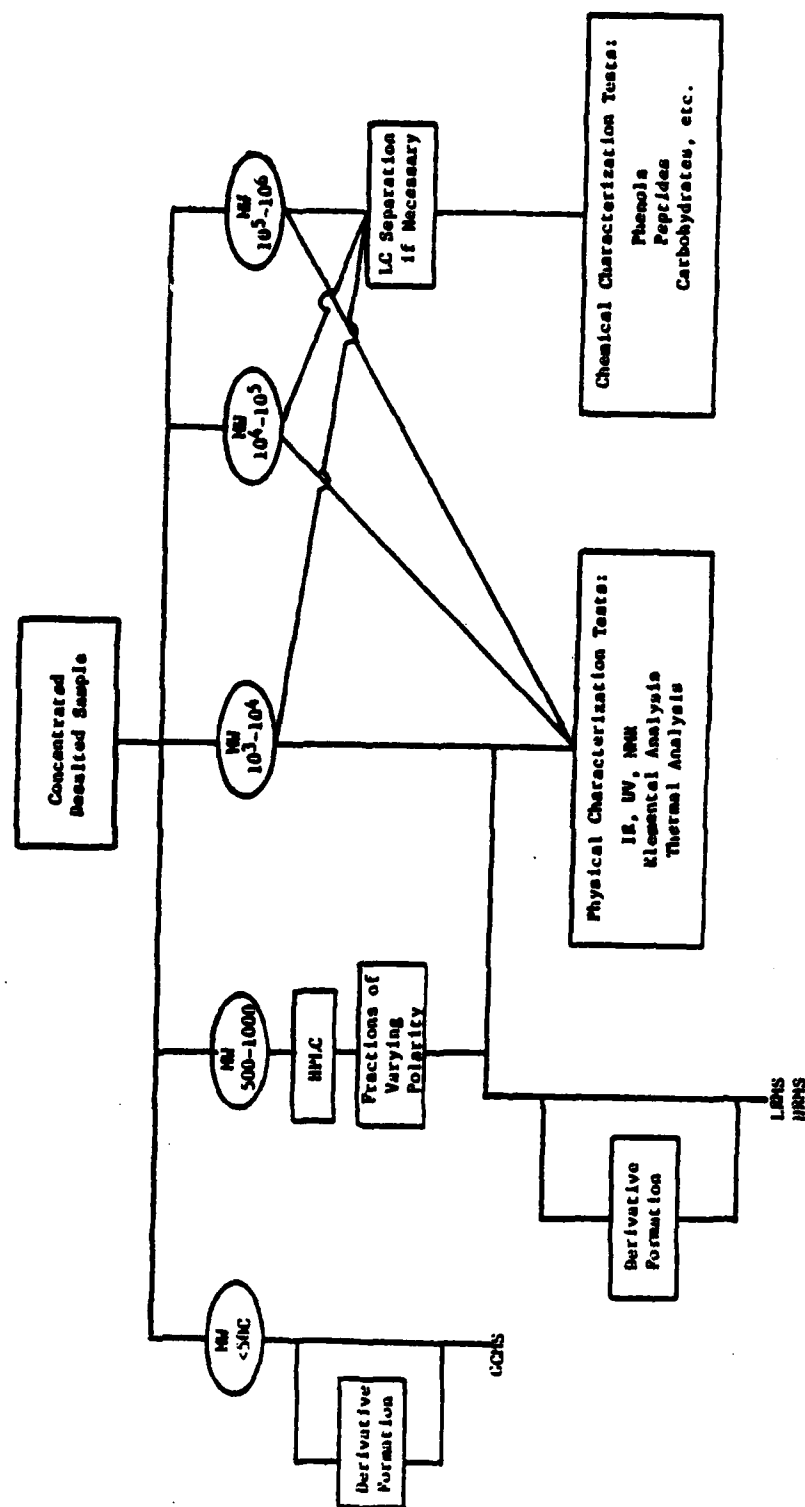


Figure 81. Candidate Protocol for Sample Fractionation/Analysis

boiling point, as well as sample component volatility.

- Separation Schemes - Organic mixtures frequently contain such a large number of components that it is difficult to interpret the data obtained from the analysis of an undifferentiated sample. Various fractionation methods appropriate to the sample and the nature of the information desired must be considered.
- Derivative Formation - Before the analysis of some samples, derivation may be required to stabilize sample components or enhance the detection limit of an analytical method.

In characterizing complex environmental samples, it is frequently necessary or desirable to perform some sample fractionation prior to analysis. Many times a separation based on physical properties is accomplished during sampling. For example, a sample of groundwater may be filtered to remove suspended sediments and salts to allow for the analysis of dissolved metals only.

Once the sample has been returned to the laboratory, a considerably larger range of separation techniques is available. Liquid column chromatography on media such as silica gel, alumina biobeads, or Florisil is often useful as a method for separating a sample into a small number (e.g., 4-8) of fractions prior to bioassay or chemical class characterization. This type of LC separation is also used to remove interferences in the analysis of selected substances. Other chromatographic procedures have been developed into high resolution instrumental methods (HPLC, GC) that are discussed under characterization. These high performance methods are frequently preferred for applications involving detailed chemical analysis. Other fractionation procedures based on physical or chemical properties of sample components include: gel filtration chromatography, membrane separation, chemical precipitations, sieving, and Bahco particle separators.

j. General Analytical Techniques

The modern analytical chemist has at his disposal a wide range of techniques for the qualitative and quantitative characterization of environmental samples. In Table 22 many of the tools which have been successfully used in these applications have been listed, along with an indication of whether their primary utility is to provide elemental composition or compound identification and whether they are primarily useful for these purposes in a broad-screen survey or specific-quantitative analysis mode. This listing distinguishes between those methods which are primarily used for the analysis of organic materials from those used principally for inorganics. These distinctions are somewhat arbitrary; RV methods can be used for

TABLE 22. ANALYTICAL TECHNIQUES

<u>Technique</u>	<u>Acronym</u>	<u>Analysis Category</u>			
		<u>Ele- ments</u>	<u>Com- pounds</u>	<u>Screen</u>	<u>Quanti- tative</u>
<u>Primarily for Organic Analysis:</u>					
1. Infrared Spectroscopy	IR		✓	✓	
2. Ultraviolet Spectroscopy	UV		✓		✓
3. Luminescence Spectrophotometry	LS		✓	✓	✓
4. Mass Spectrometry					
- Low Resolution	LRMS		✓	✓	
- High Resolution	HRMS		✓	✓	
- Automated GC/MS	GC/MS/DS		✓	✓	✓
5. Nuclear Magnetic Resonance Spectroscopy	NMR		✓	✓	✓
6. Chromatography					
- Thin Layer	TLC		✓	✓	✓
- Liquid	LC,HPLC		✓	✓	✓
- Gas	GC		✓	✓	✓
7. Combustion Analysis	C,H, etc.	✓			✓
8. Thermal Analysis	TA/TGA/DTA		✓	✓	✓
<u>Primarily for Inorganic Analysis</u>					
9. Spark Source Mass Spectroscopy	SSMS	✓		✓	
10. Optical Emission Spectroscopy	OES	✓		✓	
11. X-ray Fluorescence					
- Dispersive	XRF	✓		✓	
- Energy discriminating	EDXRF	✓		✓	
12. Neutron Activation Analysis	NAA	✓		✓	
13. Atomic Absorption Spectroscopy	AAS	✓			✓
14. Flame Emission Spectroscopy	FES	✓			✓
15. Anodic Stripping Voltammetry	ASV	✓			✓
16. Optical Microscope	OM	✓	✓	✓	✓
Scanning Electron Microscopy	SEM	✓	✓	✓	
Transmission Electron Microscopy	TEM		✓	✓	
17. Electron Diffraction	TEM/ED		✓	✓	
18. X-ray Diffraction	XRD		✓	✓	
19. Chemical Analysis					
- Anions	-		✓		✓
- Specific Analytes	-	✓	✓		✓

colorimetric assays of inorganics, as well as organics, and XRD can be applied to inorganic or organic crystalline materials. It is recognized that some methods provide adequate quantitative data in a survey mode, but the purpose of the table is to indicate the primary utility of a method.

At the onset of a task designed to characterize and treat environmental samples it is desirable to assess the applicability of each of the methods listed in Table 22. In this way, the most appropriate techniques can be utilized to ensure that all the necessary data are obtained for a given sample. The following discussion addresses both a general screening approach and the specific analytical techniques which will most likely be used in the conduct of this work.

k. General Approach to Analytical Methods

Judicious selection among the techniques available for the analysis of complex samples requires a rationale that considers both the nature of the sample and the nature of the information being sought. Different selection rationales need to be developed to meet different types of environmental objectives.

For example, the Process Measurements Branch of EPA's IERL-RTP has promulgated a set of procedures for use in Level 1 Environmental Assessment sampling and analysis (USEPA 1978). These procedures are aimed at quantifying comprehensive multimedia environmental loadings of pollutants to within a factor of two to three by using one consistent protocol. To ensure that no potentially harmful pollutant species are overlooked, the Level 1 analysis protocol places heavy emphasis on techniques that can be used in a survey mode. An overview of the Level 1 analysis scheme is given in Figure 82. The complete Level 1 evaluation, which includes biotesting as well as chemical analysis, is a tool for comprehensive screening of all significant sources. Level 1 may be supplemented or followed by Level 2 -- directed detailed analyses of specific identified pollutants, and Level 3 -- process monitoring on selected pollutants, as the need arises.

In other types of programs, particular published protocols have been specified for the determination of some contaminants, such as the EPA's list of priority pollutants. The protocols for analysis of the priority pollutants in support of the Effluent Guidelines Division of EPA have been successfully applied in our laboratories for volatile organics, base-neutral organics, acid-extractable organics, pesticides, and metals.

Other methods may also be appropriate for use in programs involving groundwater monitoring. Considerations which must always be addressed in the selection of appropriate analytical methods include:

- The Chemistry of the Analyte - The solubility of the analyte in various solvents, its boiling point, its

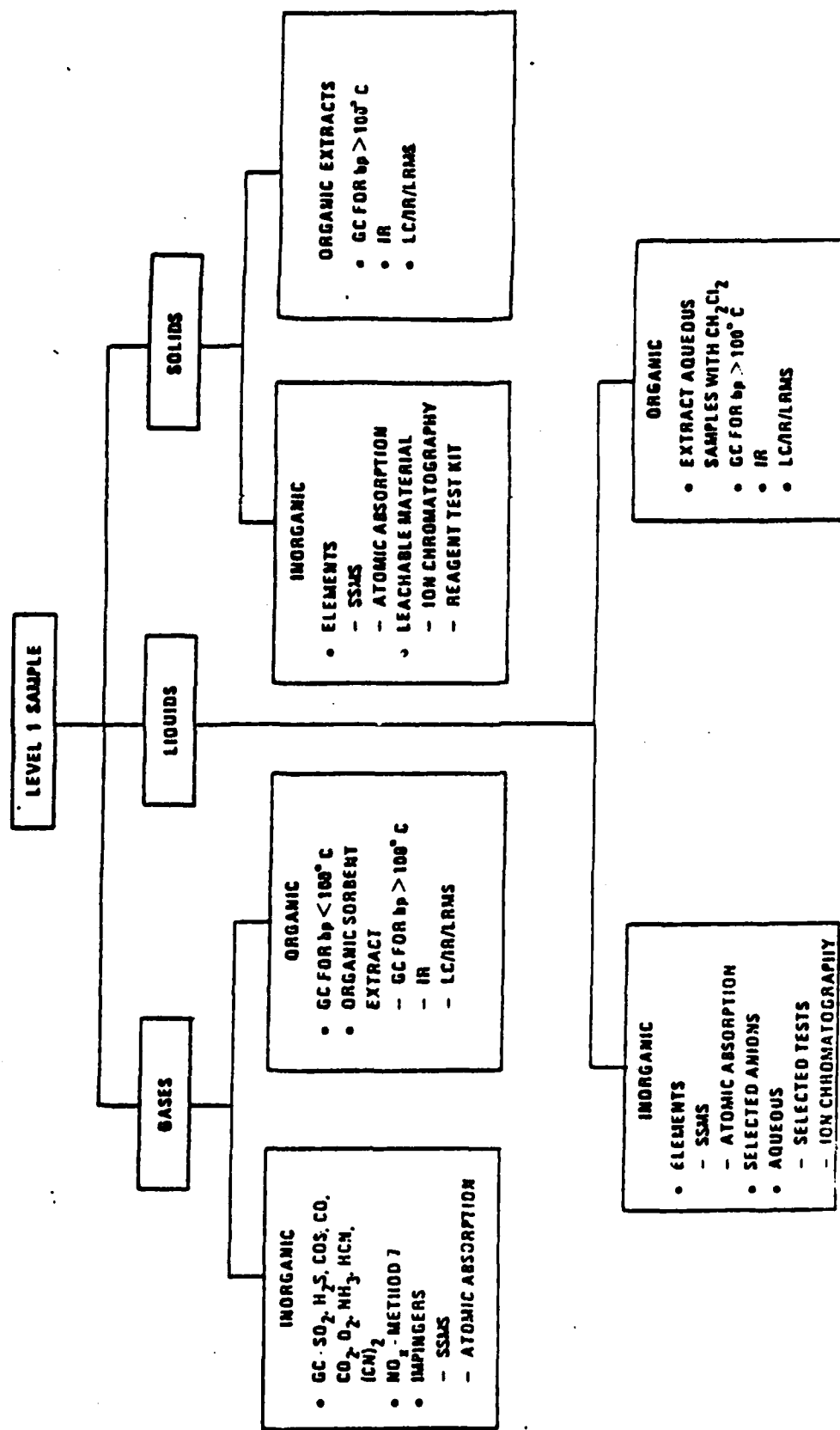


Figure 82. Multimedia Analysis Overview

Source: EPA-600-7-78-201

UV spectrum (or UV maxima) and special precautions, such as decomposition conditions.

- The Method of Detection - Analyte-specific characteristics are a major consideration in selecting the method of detection. For example, the presence of electronegative groups in the chemical makeup of an analyte makes the use of electron capture detection possible when more than one type of group is present in the analyte; the advantages of specifically detecting each will be considered.
- Extraction Considerations - Initial considerations should be given to the solvent method of detection compatibility. The solvents used to extract the analyte from groundwater samples should be compatible with the developed analytical method. For example, samples should not be extracted with methylene chloride if electron capture detection will be used.
- Limits of Detection - Decisive efforts must be made to the lowest attainable levels of detection. Methodology such as derivatization can enhance by orders of magnitude the detection of a compound, but the derivatization techniques must be reproducible.
- Statistical Requirements - Required Quality Assurance/Quality Control protocols must be followed in using or developing analytical methods.

The instrumentation necessary to determine chemical composition can be as simple as a density balance or a pH meter, or as advanced as a gas chromatograph or a mass spectrometer. Frequently, more than one method may be appropriate for the measurement at hand. One must carefully choose the equipment suitable for the task. Several considerations are important:

- Cost and availability
- Complexity of the groundwater sample
- Required sensitivity and accuracy
- Special considerations, such as trace impurities in the stream

It is often necessary to separate or resolve the component of interest from the process stream because of the lack of specificity of some instruments. In determining concentration, some property of a chemical which varies with composition is measured. For example, in measuring a solution pH (i.e., hydrogen ion concentration), the pH meter actually reads the EMF generated by the chemical potential of the hydrogen ions in the liquid. In other cases (e.g., mass spectrometry), the individual molecules themselves are detected electronically.

Because of the large number of instruments used in composition measurement, any listing is necessarily incomplete. The more important analytical tools which may be used are briefly described below.

1. Gas Chromatography (GC)

Gas chromatography is used for separation of complex mixtures of organics with appreciable volatility. GC is also an exceedingly valuable technique for quantitative analysis of sample components. With the exception of Gas Chromatography/Mass Spectrometry (discussed below), qualitative analysis of GC is limited to inferences drawn from retention times of individual peaks and known detector selectivities.

A considerable variety of detection principles have been utilized for gas chromatography purposes. Of the detectors available, several are of interest in organic analysis.

The flame ionization detector (FID) is the most versatile general purpose device. The FID responds to any substance that will burn in the air/hydrogen flame to produce ions. Most organics, except for highly halogenated species, give strong FID responses. The lower limit of detection for organic species is on the order of one nanogram per microliter (ppm) of injected solution, and the dynamic range of the detector spans four or more orders of magnitude.

The electron capture detector (ECD) is specific for species that contain electronegative atoms or groups -- halogens, phosphorus, sulfur, and nitro-groups. For example, the high selectivity of the ECD has been used to good advantage in analyses of pesticides and polychlorinated biphenyls (PCBs). The lower limit of a detection is as much as 1000 times lower than that of the FID, but the dynamic range is generally smaller. The magnitude of the ECD response is its sensitivity to analyte structure, as well as to concentrations, since different species have different electron capture cross-sections. The detector response is also temperature-dependent, and an ECD cannot usefully be employed in temperature-programmed GC. All of these factors combined support the conclusion that GC/ECD is not a technique with wide applicability in organic analysis, but one which may be used for some specific categories of analytes. Octachloronaphthalene and ethylene glycol dinitrate are examples of compounds measured successfully using electron capture detection.

The flame photometric detector (FPD) is specific for species that contain sulfur or phosphorus. Its specificity, detection limits, and sensitivity are comparable to those of the ECD, although a completely different principle of detection is involved. When operated in the sulfur mode, the FPD response is logarithmic, rather than linear, with concentration. The FPD may be utilized in organic analysis of organophosphorus pesticides and some sulfur species.

The alkali flame ionization detection (AFID) is selective for nitrogen and phosphorous species. In the alkali flame ionization

detector, a cesium bromide or rubidium sulfate salt tip is incorporated into a FID burner jet. When fuel/air flows are properly adjusted, the detector provides enhanced selectivity for phosphorus or nitrogen compounds compared to hydrocarbons. Quantitative analysis procedures for such species as nicotine and nitrosamines have been developed using the AFID. Although AFID can be used for nitro compounds, recent comparisons of detection limits for a series of explosives have demonstrated that the ECD is more sensitive for them by an order of magnitude.

The photoionization detector (PID) is specific to compounds with ionization potential of < 10.5 eV, which are ionized after absorption of UV radiation. The detector has a wide linear range and is highly sensitive to species with high UV absorptivity, such as aromatics. As little as 2 nanograms/liter of tetramethyl lead has routinely been detected using this technique.

m. Combined Gas Chromatography - Mass Spectrometry (GC/MS)

Gas chromatographic separation with mass spectrometric detection makes possible identification of GC peaks in the submicrogram sample size range. For certain specific compounds, such as polycyclic aromatic hydrocarbons (PAHs) detection limits using packed columns are in the subnanogram range (on the order of 100s of picograms). The use of capillary GC columns with their very high resolution allows separation of a number of isomeric species with detection limits 1-2 orders of magnitude lower (1-10 picograms).

The marriage of a GC/MS to a dedicated minicomputer or to an on-line data system is synonymous with the term GC/MS to many people. Computer control of the mass spectrometer during data acquisition has been enhanced by the availability of low cost microelectronic circuitry for use in the control loop. Use of GC/MS with data systems is a standard technique in both commercial and government laboratories (such as the EPA laboratories) concerned with water quality analyses. Analyses with capillary columns are only practical with automated GC/MS instruments since the typical elution peak is only about 3 seconds wide. To obtain more than a single mass spectrum in 3 seconds requires a rapid scanning mass spectrometer so that the volume of hard copy generated with a continuously operating oscillography would be unmanageable. A further advantage of these systems is in their archival and retrieval characteristics. The data recorded for any sample can be retrieved on magnetic tape, for instance, and transported to other systems. Other options, such as searching the data file of a sample for specific ions to aid in the detection, identification, and quantification of specific compounds, would be possible without a computer system for data acquisition only by rerunning the sample. Thus, automated GC/MS is rapidly developing into the method of choice for a majority of the organic analyses required with environmental samples.

n. High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography is an attractive alternative to more traditional methods, such as GC. The method's speed, sensitivity, and compatibility with aqueous systems make it an excellent candidate for use in anticipated in ground water monitoring programs.

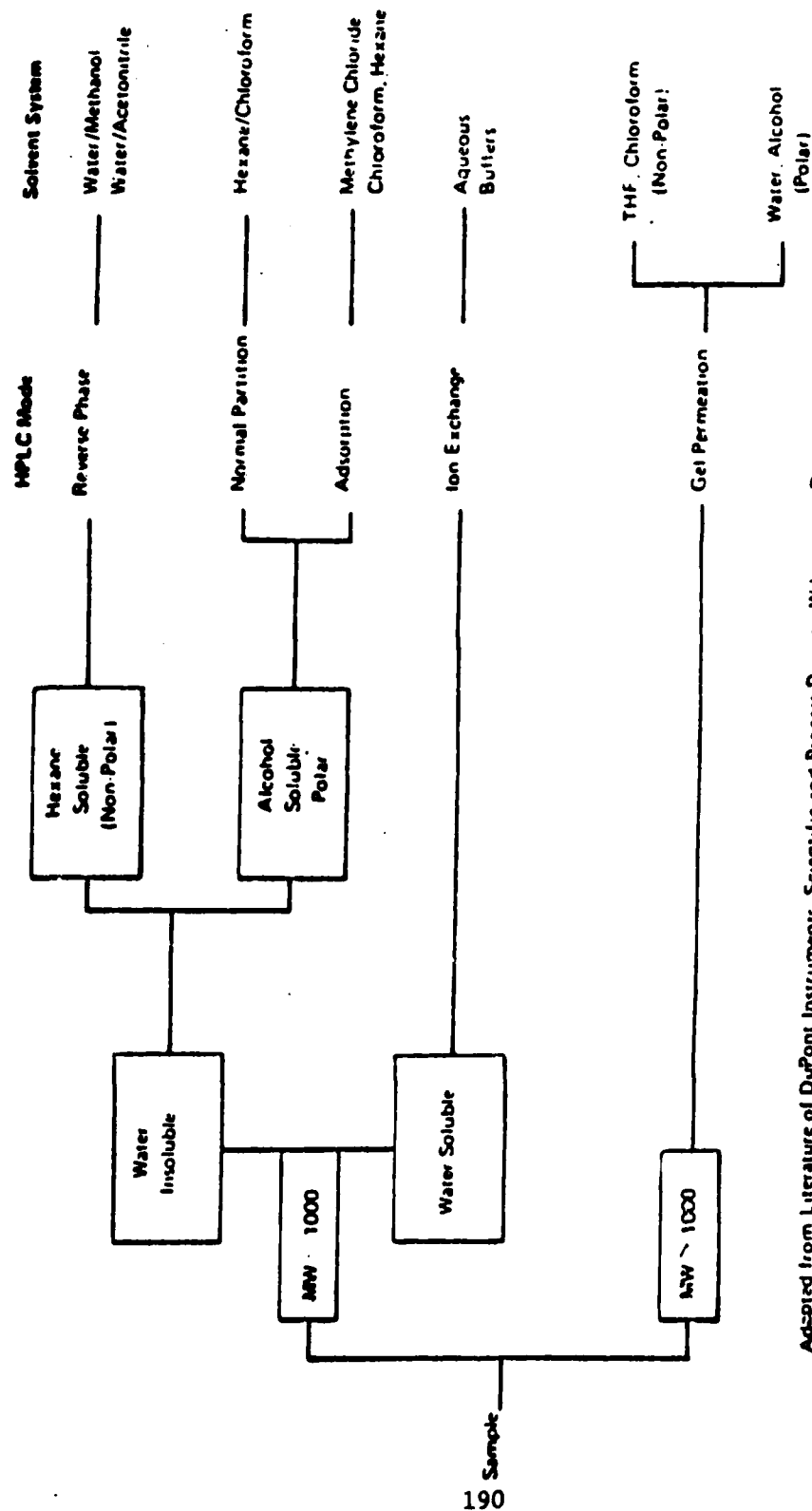
HPLC is a separation technique with applications in quantification, isolation, and identification. It is differentiated from other LC methods by high speed, high sensitivity, and high resolution comparable to that of gas chromatography. These improvements have been achieved by columns using microparticulate packings with small diameter (5-50 micrometers) and high surface area (approximately 300 m²/g particles). Separation may be achieved by differences in molecular size, number of types of functional groups, steric configuration, polarity, etc.

HPLC methods are likely to be used in one of two modes: normal or reverse phase. Reverse phase HPLC is based on separation by polarity differences in the mobile vs. stationary phase. The stationary phase is prepared by using long-chain alkyl silylating reagents to produce a hydrophobic layer on a silica solid substrate. Nonpolar solutes have a higher affinity for the stationary phase than do polar solutes. The mobile phase is generally programmed in a continuous gradient elution scheme from polar to nonpolar solvents. Water/methanol and water/acetonitrile are binary solvent systems frequently employed. In reverse-phase HPLC, polar sample components elute first. Normal HPLC, like reverse-phase HPLC, is based on separation by polarity. In normal phase separations, the stationary phase is more polar than the mobile phase. Gradient elution systems from nonpolar to polar solvents are used, and nonpolar solutes elute first. A guide to the selection of an analytical HPLC method is summarized in Figure 83.

The two most commonly used methods for detection of sample components in HPLC effluents are ultraviolet (UV) absorbance detectors and refractive index (RI) detectors. High sensitivity and specificity are achievable using a UV detector at fixed (e.g., 254 nm) or variable 200-800 nm wavelength. Lower limits of detection in the nanogram range have been reported for strongly absorbing sample species (i.e., molar absorptivity ~ 14,000).

The differential refractometer detector has lower sensitivity and less specificity than the UV detector. The RI detector responds to essentially all sample components and is a potential "universal" detector for HPLC, but lower limits of detection are in the microgram range. Furthermore, generality of the RI detector response requires matching of solvent system refractive indices during gradient elution HPLC; this is difficult to achieve in practice.

A third type of detection system is the spectrofluorometer. This fluorescence detector affords greater sensitivity and selectivity than UV does for those compounds which fluoresce. The specificity of this detector does limit its applicability in detecting a great number of



Adapted from Literature of DuPont Instruments, Scientific and Process Division, Wilmington, Delaware

Figure 83. Guide to Selection of HPLC Analytical Procedures

organic compounds. However, its use can be extended by the use of fluorescent reagents, such as Fluorescamine (4-phenylspiro[furan, 2H-1-phthalan]3'3-dione) and Fluoropa (o-phthalaldehyde). These reagents react with primary amines to produce highly fluorescent derivatives.

Another type of detection system which may be useful is the electrochemical detector (EC). Electrochemical detection is a sensitive and selective method which will recognize a particular substance depending on the ability of the compound to be oxidized or reduced, and on the nature of the electrode and the mobile phase. Selectivity for one component of a mixture, as compared to another, may be achieved by adjusting the potential of the electrode.

o. Mass Spectrometry

- Low Resolution (LRMS) - Low resolution mass spectrometry is perhaps the single best technique to use to examine an unknown sample to determine whether or not organic compounds are present. In cases of simple mixtures, the LRMS data may be sufficient for compound identification, especially using modern file-searching techniques.
- High Resolution (HRMS) - High resolution and specific ion detection mass spectrometric techniques used in conjunction with data acquisition and processing have the ability to identify elements and compounds in the 10^{-9} - 10^{-12} g range with freedom from false positive results. Relatively uniform high sensitivity is obtained for all materials which are volatilizable at source temperatures and pressure. The technique is restricted to volatile material and usually excludes low polymers or salts, etc. A tremendous amount of data are present in the HRMS of an organic environmental mixture, and much of the value of the data lies in evolving a unique means of data reduction. A scheme based on an analysis of the chemical types present in a sample has been developed at Arthur D. Little, Inc., by Caragay et al. HRMS appears to have its greatest promise in determining the elemental composition of trace organic constituents in a sample and in verifying the absence of certain sought species.
- Infrared Spectroscopy (IR) - IR is a general technique for group type characterization of samples. Virtually every organic and inorganic species of interest has at least one absorption frequency in the normal IR range. The technique is widely available in most laboratories and is capable of detecting less than 10 micrograms with modern attachments. The method is most attractive for its

nondiscrimination and assurance that every major component of the sample will be represented in the spectrum. Species present at less than 5 - 10 percent in the mixture will generally not be detected. Combustion source samples which are black will suffer from low transmission and resolution because of black-body adsorption effects. However, the new Fourier transform technique has helped overcome some of these problems.

- Nuclear Magnetic Resonance Spectroscopy (NMR) - NMR has not been extensively used in environmental analyses to date, primarily because of the high purity, liquid character, and large sample sizes which had been a requirement of older instruments. The introduction of Fourier Transform Nuclear Magnetic Resonance Spectrometers and the availability of Magic Angle Spinning probes has eliminated these earlier constraints. New environmental applications of NMR techniques are being developed and show particular promise for the characterization of fuels and solid effluent streams.

p. Ion Chromatography (IC)

Ion chromatography (IC) is a separation and analysis technique which was recently developed for analysis of cations and anions. The technique involves use of a low capacity ion exchange resin column for separation, followed by another column designed to suppress the conductivity of the background electrode prior to detection of the ions of interest by means of a conductivity detector. The method of analysis is selective and sensitive, especially for many ionic species which cannot otherwise be detected by the usual ultraviolet or visible absorption photometric or refractive index liquid chromatographic detectors. Analysis of alkali and alkaline earth metals, aliphatic amines, ammonia, and many anions, including $\text{P}_2\text{O}_7^{4-}$, NO_3^- , S^{2-} , AsO_4^{3-} , carboxylates and sulfonates, has been achieved in complex aqueous mixtures. Detection limits have been around the high ppb region with a precision of less than 5 percent for most species. Incorporation of a preconcentrator column has increased sensitivity to less than 2 ppb for anions such as Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} . This allows rapid and accurate analyses of many species which previously could only be performed using ion-specific electrodes and wet chemical methods on an individual ion basis.

q. Atomic Emission Spectroscopy (AES)

Multielement analyses can be performed with the AES. Qualitative analysis for most elements can be performed by recording the entire emission spectrum of a given sample and inspecting for the presence or absence of emission lines corresponding to elements of interest. This

may be especially useful, for example, for screening of samples for subsequent quantitative analysis.

Detection limits are, in general, comparable or superior to those obtained using conventional flame atomizers and atomic absorption spectroscopy. For certain elements (e.g., Ti), detection limits are several times lower than those obtained using the most sensitive atomic absorption techniques. Certain nonmetals (e.g., P and B) can be easily determined directly in solution with good sensitivity, thus eliminating the need for time-consuming colorimetric methods. In addition, many of the matrix or interelement effects noted in other techniques are absent, and high dynamic concentration ranges are usually obtained.

These advantages may make atomic emission spectroscopy a singularly time- and cost-effective approach to the analysis of certain complex samples.

r. Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy is one of the most widely used analytical techniques when information on one or a few specific elements is required. Approximately 70 elements can be determined. With appropriate modifications, such as sample preconcentration, electro-thermal atomization, or atomization of gaseous hydrides, very low detection limits have been obtained for many elements.

The advantages of AAS which, in addition to broad applicability and low detection limits for many elements, include relative ease of sample preparation, standardization, operation, and moderate costs, have led to its widespread acceptance as a standard method for application to quantitative analysis of many element.

Some examples of these types of analyses are:

- Combustion Analysis - Classical combustion analysis for the determination of elements such as C, H, N, S, etc., requires large amounts of sample (10 - 50 mg) compared with the instrumental methods. However, it is probably the best means of obtaining the data needed for a total mass balance analysis of a sample. This could be supplemented by an ignition analysis (loss on ignition at 550°C, volatiles content) for inorganic content, but this latter method suffers from inaccuracies in unknown environmental samples.
- Thermal Analysis (TA, TGA, DTA) - Instrumental thermal analyses techniques have substantial sensitivity for the characterization of the thermal behavior of small amounts of sample. Although these procedures lack the specificity of other methods in the determination of elements or compounds, they can

be of use in qualitatively and quantitatively comparing environmental samples with regard to parameters such as ash content.

- Spark Source Mass Spectroscopy (SSMA) - Spark Source excitation is usually used for elemental analysis of environmental samples because of the relatively uniform ion formation for all elements. Sample preparation, including removal of organic matter and mixing with graphite to prepare electrodes, is required prior to analysis. Standards prepared in a matrix similar to the sample are required for quantitative analysis. High molecular weight organics can interfere in this analysis.
- X-ray Fluorescence (XRF) - All elements with an atomic number greater than 11 can be analyzed by XRF, although satisfactory data are lacking for elements with atomic numbers greater than 20. Quantitative comparisons of energy discriminating and wavelength dispersive techniques have been published. XRF is dependent on particle size effects and sample thickness. For airborne particulate analysis, XRF works best when samples² are deposited on surfaces. Only ngs of elements/cm² of deposit are required. Little or no sample pretreatment is required, and the technique is nondestructive.
- Neutron Activation - Neutron activation analysis has excellent sensitivity for certain elements and is applicable to a wide variety of matrices. It is especially convenient for analyzing filters in which sample deposition is not confined to the surface. Extensive auxiliary facilities and long turnaround time are required for certain elements. No sample pretreatment is required.
- Flame Emission Spectroscopy - Lower sensitivities than those obtainable by flame atomic absorption and fluorescence techniques may be obtained for certain elements by flame emission methods. Simultaneous multielement analysis is possible, since a separate source is not required for each element (or groups of a few elements) as in atomic absorption. However, flame emission methods are critically dependent on flame conditions, and optimum excitation conditions vary for different elements. Many modern AA instruments have flame emission capability, and it is likely that such hybrid instruments may be required for situations calling

for the widest possible scope at the highest possible sensitivity.

- Differential Pulse Anodic Stripping Voltammetry - Sensitivities comparable to nonflame AA techniques are obtained for certain metals with DPASV. The method is limited to the determination of approximately twenty metals which are soluble in mercury; the majority of applications have dealt with about ten of these. Approximately 4 - 6 elements may be determined in a single sample. The technique may be nondestructive.
- Microscopy - Microscopic techniques are especially useful for the examination of particulate matter. Information on compounds present, elemental composition, and crystalline form may be obtained rapidly on very small samples. Lower detection limits are 10^{-12} g with the light microscope, 10^{-15} g with the scanning electron microscope, and 10^{-18} g with the transmission electron microscope. Energy dispersive X-ray fluorescence and X-ray diffraction analysis may be used in conjunction with the latter two microscopic techniques to determine the chemical composition of tiny single particles. The light microscope is one of the most powerful simple techniques although frequently overlooked because of lack of personnel training.
- Electron Diffraction - This technique, used in conjunction with a transmission electron microscope, is extremely powerful for crystal identification when only minute amounts of solid are available. However, extensive sample preparation is necessary, and the method is not likely to be viable for most environmental samples. One severe problem is that many analyses are necessary to represent a heterogeneous sample.
- X-ray Diffraction - This method is very powerful for the positive identification of crystalline species. Computer programs have recently been written which allow the simultaneous identification of up to 10 compounds in a mixture if the patterns of those compounds are present in the data file. Unfortunately, many environmental samples suffer the problem of having compounds present in amorphous forms and at various degrees of hydration. While the technique is sensitive and precise, it will probably only be applicable to a limited range of samples.

- Anion Measurements - For a screening program of the type in which an accuracy of a factor of 2 or so is acceptable for the analysis of samples of widely varying composition, the use of specific ion electrodes is strongly recommended wherever practicable. Since the electrodes give a (generally) linear response over several orders of magnitude, the need for further sample manipulation of off-scale samples (i.e., dilution [taking a different aliquot] changing cells), such as is experienced in narrow-band width measurement techniques (i.e., colorimetry, titrimetry) is eliminated. Colorimetric techniques may be required in some cases where highly precise determinations of trace anions are required. Acid-base and redox titrations can be applied in specific instances, but these procedures are generally not well suited for trace analyses.

a. Total Organic Carbon (TOC) and Total Organic Halogens (TOH)

The total organic content in groundwater samples may be determined by a number of different commercially available total organic carbon analyzers (total organic halogens may be of use in those cases where halogenated species are of interest). The organic carbon present in a sample is typically converted to methane (CH_4) or carbon dioxide (CO_2) using reduction, oxidation, or pyrolysis techniques. The products are subsequently measured using nondispersive infrared, flame ionization, conductivity, or similar techniques. Detection limits vary from low ppb to low ppm levels.

SECTION V

PREDICTION OF CONTAMINANTS TRANSPORT

1. PHYSICAL, CHEMICAL, AND BIOLOGICAL PARAMETERS AND CONSTANTS APPLICABLE TO ORGANIC CONTAMINANTS AND PHYSICAL SYSTEMS OF CONCERN

a. Overview

Models designed to predict the fate and transport of organic chemicals in soil/groundwater systems will usually require a variety of parameters and constants to properly address two questions:

- (1) Mobility: How easily is the chemical mobilized (i.e., transported) through the important subcompartments, e.g., soil, soil air, and soil water?
- (2) Persistence: How easily is the chemical degraded by such processes as biodegradation, hydrolysis, or oxidation?

Associated with the answers to these questions are a number of chemical-specific and environment-specific properties. Tables 24 and 25 provide a summary list of the most important chemical-specific and environment-specific properties.

Many of the chemical-specific parameters (or "constants") are functions of one or more of the environment-specific parameters (and the nature of the waste) and thus are not true constants. For example, the rate of hydrolysis may be strongly affected by temperature, pH, the presence of catalysts (e.g., certain heavy metal cations), and chemical concentration. Similarly, there are some environment-specific parameters that will be functions of the chemical, primarily when the chemical (or waste) is present in significant concentrations. For example, the soil porosity, groundwater pH and soil microbiological population will be affected by the presence of many chemicals.

The list of important properties provided in Tables 23 and 24 would, along with the requirement that their variability be known, appear to place an excessive burden on a rigorous modeling effort. There are, however, a few ways in which the burden can be reduced. First, an initial prescreening of the site and chemical(s) of concern will frequently allow a determination that one or more transport or degradation pathways will be of little concern. For example, if the contamination incident involves low concentrations (in groundwater) of a highly soluble, refractory compound, then the volatilization and biodegradation pathways might be neglected in the model. This, in turn, removes the requirement for obtaining the chemical- and environment-specific properties associated with these pathways (e.g., Henry's law constant, diffusion coefficient in air, rate of biodegradation, and wind/air parameters).

TABLE 23. IMPORTANT CHEMICAL-SPECIFIC PROPERTIES

Bulk (Condensed Phase) Properties Affecting Mobility^a

Physical state (liquid or solid) of waste
Chemical composition of waste
Density (liquid)
Viscosity (liquid)
Interfacial tension (with water and minerals) (liquid)
Water solubility
Vapor Pressure

Properties to Assess Mobility of Low Concentrations^b

Soil adsorption coefficient
Henry's law constant (or vapor pressure and water solubility)
Diffusion coefficient (in air)
Acid dissociation constant

Properties to Assess Persistence^c

Rate of biodegradation (aerobic and anaerobic)
Rate of hydrolysis (and/or elimination)
Rate of oxidation or reduction

Notes to Table 23

- a. These properties will be important when it is known or suspected that a separate organic phase exists in the soil/groundwater system.
- b. These properties are important in assessments of the mobility of chemicals present in low concentrations (i.e., not as a separate phase) in the soil/groundwater system.
- c. For these properties it is generally important to know: (1) the effects of key parameters on the rate constants (e.g., temperature, concentration, pH); and (2) the identify of the reaction products.

TABLE 24. IMPORTANT ENVIRONMENT-SPECIFIC PROPERTIES

Soil Properties^a

Porosity (air filled and total)
Moisture content (in unsaturated zone)
Particulate surface area (area per unit weight)
Organic carbon content (weight percent basis)
pH
Cation exchange capacity
Temperature
Microbiological population density (and type(s))
Nutrient availability
Gas generation rate (esp. for landfills)

Leachate/Groundwater Properties

pH
Total dissolved solids, total dissolved carbon, and
concentration of other major constituents and/or
potential catalysts
Groundwater flow rates

Meteorological Factors

Infiltration rate
Evapotranspiration rate
Windspeed and direction (wind rose)
Air temperature and pressure

Notes for Table 23

- a. If possible, values of these properties should be available for various depths, locations, seasons, etc., in the area of concern.

A second way to reduce the data generation burden (for chemical-specific properties) is to use estimates (see, for example, Lyman et al., 1982) or surrogates. In either case, sensitivity analyses could be run on the selected model to determine if the output was significantly affected by the uncertainty in the inputs.

A detailed discussion of all of these properties, their environmental significance and variability, common methods of representation and units, and measurement methods is beyond the scope of this section.

2. CHARACTERISTICS OF INITIAL MIXING

The initial mixing of an (organic) pollutant with groundwater will have characteristics that will depend in complex ways on several variables including: (1) the time and space scales associated with the source release; (2) chemical-specific parameters; and (3) environment-specific parameters. We know of very few studies of this subject (especially for large, rapid releases into the soil/groundwater system) and the field engineer can only expect limited help from the available data generated by models, or from case histories of similar incidents.

Key questions associated with the characterization of initial mixing are:

- a. Was enough material released to result in the probable existence of a distinct organic phase in the soil/groundwater system?
- b. If so, where is this "second phase" material likely to be?
- c. How long will the "second phase" material persist?
- d. To what extent will groundwater be contaminated by this material?

Partial answers to these questions are given in the discussion below.

Time and space scales associated with the pollutant's release will be partial determinants of how much groundwater (area) is affected and to what degree. Time scales may range from minutes to hours on the short end (e.g., a one-time spill or leak from a container) to years at the long end (e.g., a slow leak through a liner or pipe). Space scales may range from a few square meters (for a point source leak) to several hectares (for large lagoons, pesticide application areas, or runoff). Clearly, a large release over a small time and/or space scale will have a greater potential for the formation of an distinct organic (second) phase in the soil/groundwater system immediately beneath the release site.

How quickly pollutants are transported down through the unsaturated soil zone to groundwater will depend on a variety of chemical- and environment-specific factors (see Section V). The rate of transport can probably be predicted reasonably well only when a second phase does not exist so that percolation with water is the dominant transport mechanism. In such cases, when the percolating water reaches the groundwater, mixing involves simple dilution.

The spill or release of bulk quantities of any liquid organics will, in most cases, have a high probability of resulting in the formation of a second (organic) phase near the groundwater table. Numerous case histories (e.g., from the rupture of storage tanks and leakage from unlined chemical dumpsites) have demonstrated this phenomenon.

There may be, in some cases, sufficient chemical- and environment-specific data to allow a prediction of the relative probability (or speed) of such second phase movement. Some of the more important factors are listed below.

Factors Enhancing the Mobility of Second Phase
Organic Material Through the Unsaturated Zone.

<u>Chemical-Specific</u>	<u>Environment-Specific</u>
High density	High soil porosity or fractures
Low viscosity	Low organic matter content of soil
Low interfacial tension	Low particle surface area
Persistent (i.e., resistant to degradation by hydrolysis, etc.)	Shallow depth to groundwater
Low soil adsorption coefficient	

If and when a second phase of organic material does reach the groundwater table, the initial mixing characteristics are likely to be a function of the following parameters:

- Density difference between the organic material and groundwater;
- Water solubility of the second phase material;
- Slope of groundwater table and flow rate of groundwater; and

- Reactivity of organic material with water (esp. rate of hydrolysis)

Material that is denser than water (e.g., chlorinated solvents) may continue to sink down through the saturated soil zone leaving a near-vertical trail of contaminated soil and groundwater. A plume of contaminated groundwater deeper than usual is the likely result.

Material that is less dense than water (e.g., most hydrocarbon fuels) will tend to spread out over the groundwater table and, in many cases can flow in directions different from the local groundwater flow.

Irrespective of the density, the rate of dissolution of the chemical in groundwater will depend primarily on the chemical's water solubility, the contact area, and the groundwater flow in the area. In areas where groundwater movement is especially slow, molecular diffusion (of the chemical through water) may limit the rate of the dissolution process. A separate second phase of organics could persist for months to years in situations where the quantity released was large, the chemicals' solubility was low, the groundwater movement slow, and/or the area of contact was small.

In those cases where the material initially released to the soil/groundwater environment contained a mixture of different chemicals, one should expect a chromatographic effect. That is, chemicals with higher water solubility and lower soil adsorption coefficients will be transported more rapidly through both the unsaturated and saturated soil zones. Some of the more volatile components of the mixture may be transported up (through the unsaturated zone) to the soil surface. Such effects have been demonstrated in laboratory tests using kerosene and gas oil (van der Waarden et al., 1977 and 1971).

3. MATHEMATICS OF DISPERSION, DIFFUSION, AND DILUTION

a. Introduction

When two miscible fluids are brought into contact, there is an initial sharp interface between them which vanishes into a transition zone between the two fluids. As a solute is transported in a groundwater flow system, it gradually spreads and occupies an ever increasing portion of the flow domain. This spreading phenomenon that causes dilution of the contaminant is called hydrodynamic dispersion. Hydrodynamic dispersion occurs because of mechanical mixing during fluid advection and because of molecular diffusion due to the thermal-kinetic energy of the solute particles. Figure 84 illustrates the dilution process caused by mechanical dispersion. At high groundwater velocities, such as would occur in relatively permeable material (i.e., sand or fractured bedrock), mechanical mixing is principally responsible for dispersion. At low groundwater velocities, such as would exist in a clay or shale, molecular diffusion is principally responsible for fluid mixing. The two processes which make up hydrodynamic dispersion,

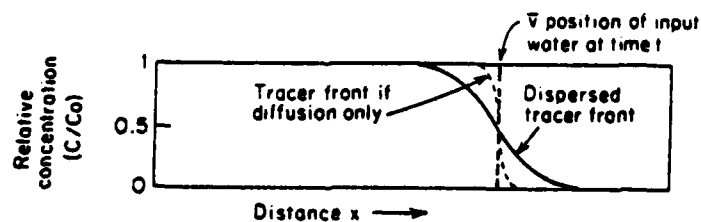


Figure 84. Schematic Diagram Showing the Contribution of Molecular Diffusion and Mechanical Dispersion to the Spread of an Originally Sharp Concentration Front.

Source: Freeze and Cherry, 1979.

mechanical mixing and diffusion, will be discussed separately, then the combined effect of hydrodynamic dispersion and groundwater flow in the transport of solutes will be discussed.

(1) Mechanical Mixing

Mechanical mixing, or mechanical dispersion as it is sometimes called, is a mixing process, and it has a similar effect as turbulence in a surface-water regime. On a microscopic scale, it is caused by three mechanisms:

- dispersion due to differential velocity across a pore channel due to irregular pore surfaces,
- dispersion due to different pore velocities resulting from differences in pore size, and
- dispersion due to the tortuosity, branching and interfingering of pore channels.

(2) Diffusion

Diffusion is the process whereby ionic or molecular constituents move under the influence of their kinetic activity in the direction of their concentration gradient. It can occur in conjunction with mechanical dispersion or it can occur in the absence of any bulk hydraulic movement of the solution. Diffusion ceases only when concentration gradients are nonexistent. This process is sometimes referred to as molecular diffusion or ionic diffusion.

Fick's first law states that the mass of a diffusing substance passing through a given cross-section per unit time is proportional to the concentration gradient and is expressed as:

$$F = -D \frac{dC}{dX} \quad (11)$$

where:

F is the mass flux per unit area per unit time,

D is the diffusion coefficient,

C is the solute concentration,

$\frac{dC}{dX}$ is the concentration gradient.

In porous media, the diffusion coefficient, D, is replaced by an empirically derived "apparent diffusion coefficient," D_a , which is represented by the relation

$$D^* = AD \quad (12)$$

where A is an empirical coefficient, less than unity, that takes into account the effect of the solid phase of the porous medium on the diffusion.

Fick's second law relates the concentration of a diffusion substance to space and time and is given by

$$\frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} \quad (13)$$

Solution to equation (12) is given by

$$C_1(x,t) = C_0 \operatorname{erfc} \left(\frac{x}{2\sqrt{D^* t}} \right) \quad (14)$$

where:

$C_1(x,t)$ is the concentration of species 1 at location x and time t,

C_0 is the source concentration of species 1, and

erfc is the complementary error function

b. Contaminant Transport Processes

The principles involved in developing the fundamental differential equation for contaminant transport are described in Bear (1972), Freeze and Cherry (1979), and Fried (1975). This transport equation is developed by applying the principles of conservation of mass to the convection of a contaminant in a dispersive porous medium in which chemical sorption occurs.

For an elemental volume, this conservation of mass statement can be written as

net rate of change of mass of solute within the element	=	flux of solute out of the element	-	flux of solute into the element	±	loss or gain of solute mass due to reactions
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Mathematically, this can be written in one-dimensional form as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} + \frac{1}{n} \frac{\partial q^*}{\partial t} \quad (15)$$

where:

C is the solute concentration
 D is the dispersion coefficient
 V is the average linear pore velocity
 n_{*} is porosity, and
 q is the mass of solute transferred to or from
 the solid phase

For nonreactive species, the last term on the right-hand side of equation (15) is zero, and the equation is called the advection-dispersion equation. Analytical solutions for one-, two-, and three-dimensional representations of the advection-dispersion equation are given by Bear (1972), Fried (1975), and many others. The use of numerical methods to solve this equation is reviewed by Anderson (1979).

Understanding contaminant hydrology requires obtaining quantitative or semiquantitative estimates for each of the terms in equation (15). Simulation of real contaminant migration patterns using mathematical models requires representation of Equation (15) in two or three dimensions in a formal sense. For persons confronted with the field problem of defining the areal extent of contaminant plumes using test drilling and piezometers or monitoring wells, it is the combined result of all of the processes described in Equation (15) that is important.

The remainder of this section will focus on the physical significance of the terms in Equation (14), excluding the chemical reaction term. To do this, we will follow the description in Freeze and Cherry (1979) and focus on homogeneous and heterogeneous media.

(1) Nonreactive Species in Homogeneous Media

The one-dimensional form of the advection-dispersion equation can be written as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left(D \frac{\partial C}{\partial X} \right) - V \frac{\partial C}{\partial X} \quad (16)$$

where all terms are as defined previously.

As discussed earlier, the coefficient of hydrodynamic dispersion can be expressed in terms of two components, mechanical dispersion, and molecular diffusion. Laboratory experiments (Cherry *et al.*, 1975; Bear, 1972) have shown that the dispersion coefficient can be represented by

$$D = a_L V^n + D^* \quad (17)$$

where:

- D is the dispersion coefficient
- a_L is the longitudinal dispersivity of the medium
- V is the average linear pore velocity
- m is an experimentally derived parameter, usually close to unity,
- D^* is the apparent diffusion coefficient

The effect of the dispersion coefficient is to cause some of the contaminant to move faster than the average linear velocity of the groundwater and some of the contaminant to move slower than the average linear velocity. This results in a smearing out and dilution of an originally sharp boundary between contaminated and noncontaminated water. Figure 84 illustrates the combined effect of molecular diffusion and mechanical mixing to the spread of a concentration front.

The dispersion process causes spreading of the contaminant species in directions transverse to the flow path, as well as parallel to it. Figure 85 illustrates the lateral spreading due to transverse dispersion.

Solutions to one-dimensional flow problems are useful in the interpretation of laboratory column experiments, but are somewhat limited in application to field problems. Baetsle (1969) describes a method for obtaining preliminary estimates of the migration patterns that may arise from small contaminant spills or from leaching of buried wastes.

Assuming the contaminant originated as an instantaneous slug at a point source, the concentration at time t is given by

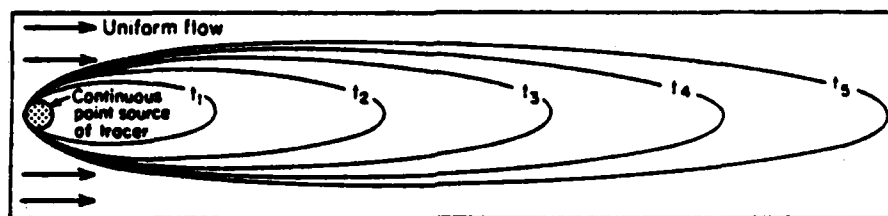
$$C(X,y,z,t) = \frac{M}{8(\pi t)^{1.5} \sqrt{D_x D_y D_z}} \exp \left(-\frac{X^2}{4D_x t} - \frac{Y^2}{4D_y t} - \frac{Z^2}{4D_z t} \right) \quad (18)$$

where:

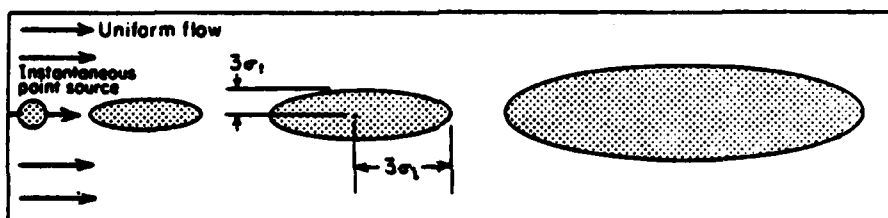
- M is the mass of contaminant introduced at the point source
- D_x, D_y, D_z are directional dispersion coefficients, and
- X, Y, Z are distances from the center of gravity of the contaminant mass

The peak concentration that occurs at the center of gravity of the contaminant plume is given by

$$C_{\max} = (C_o V_o / (8(\pi t)^{1.5} \sqrt{D_x D_y D_z})) \quad (19)$$



(a)



(b)

Figure 85. Two-Dimensional Spreading of a Contaminant in a One-Dimensional Flow Field in a Uniform Sand. (a) Continuous Contaminant Source, (b) Instantaneous Contaminant Source.

Source: Freeze and Cherry, 1979.

where:

C_{\max} is the maximum concentration at center of plume
 C is the initial concentration, and
 V_0 is the initial volume

The other terms are as defined previously. The zone in which 99.7 percent of the contaminant mass occurs is described by

the ellipsoid with dimensions $3\sigma_x = \sqrt{2D_x t}$, $3\sigma_y = \sqrt{2D_y t}$, and $3\sigma_z = \sqrt{2D_z t}$, where σ is the standard derivation of concentration (see Figure 85).

In complex hydrogeologic environments, these equations are of limited value because they do not consider the heterogeneity of the system. In relatively simple settings, however, they can provide preliminary estimates of migration patterns.

(2) Nonreactive Species in a Heterogeneous Media

The heterogeneity of natural materials complicates the problem of predicting and detecting contaminant behavior in groundwater flow systems. Contaminant transport is affected by both large scale and small scale heterogeneities. The larger scale heterogeneities, such as are caused by variations in geologic units, affect the general groundwater flow patterns. The smaller scale heterogeneities affect the dispersion of the contaminant.

Groundwater flow follows the path of least resistance and in a multilayered flow system most of the fluid flow will occur in the more permeable units with less flow occurring in the less permeable units.

Figure 86 illustrates the effect on the large-scale flow system and, hence on contaminant transport of stratification. These relatively simple variations can cause complex variations in the contaminant distribution pattern. Actual conditions are generally more complicated than these simple examples, and the end result is that one should expect the contaminant plume to have a very complex geometry.

On a smaller scale, the variations between different zones of the same layer can create a significant amount of dispersion of the contaminant front. Variations in the relative percentages of sand, silt, clay, and cementation or fracturing create local variations in permeability. These local scale variations are sufficient to cause fingering and spreading of the contaminant front. Figure 87 illustrates the effects of small scale heterogeneities on the pattern of contaminant migration in granular porous media. In Figure 87, the continuous higher permeability layers have allowed the contaminant front to advance more rapidly than in the lower permeability layers. In Figure 87, the

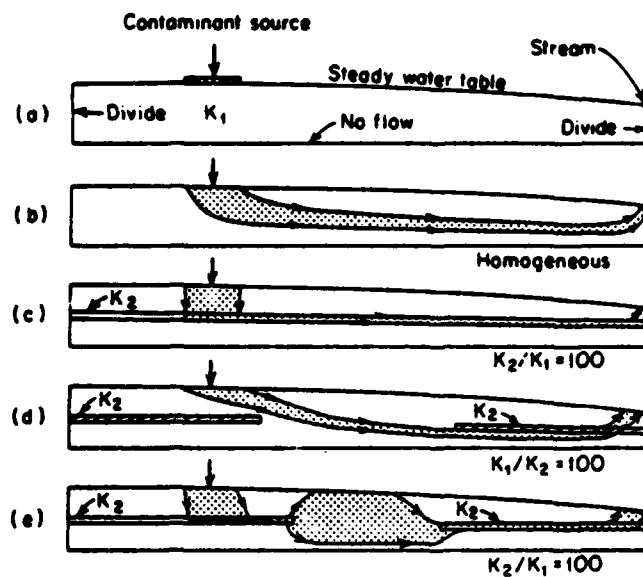


Figure 86. Effect of Layers and Lenses on Flow Paths in Shallow Steady-State Groundwater Flows Systems. (a) Boundary Conditions, (b) Homogeneous Case, (c) Single Higher-Conductivity Layer, (d) Two Lower-Conductivity Lenses, (e) Two Higher Conductivity Lenses.

Source: Freeze and Cherry, 1979.

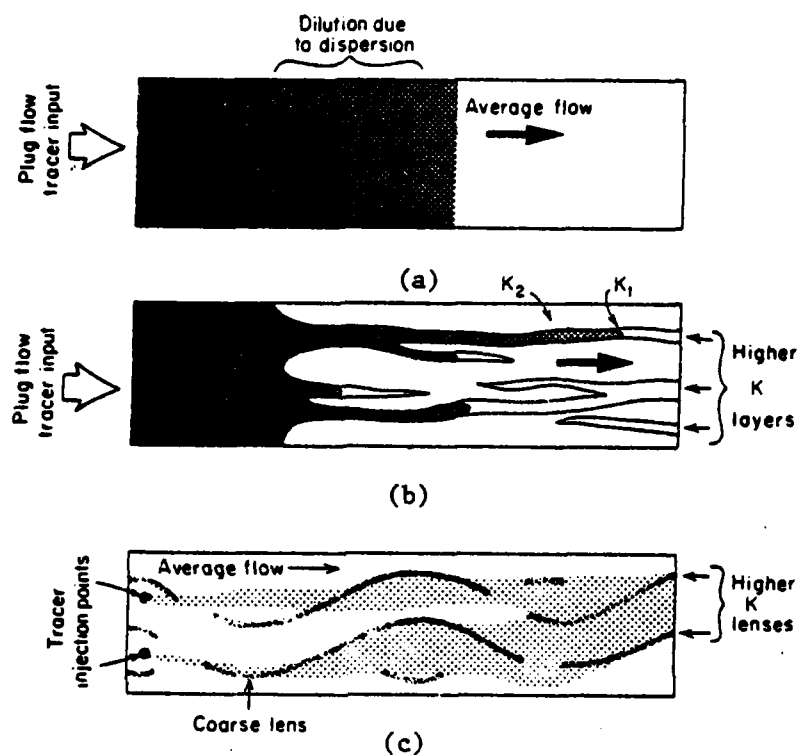


Figure 87. Comparison of Advance of Contaminant Zones Influenced by Hydrodynamic Dispersion. (a) Homogeneous Granular Medium, (b) Fingering caused by Layered Beds and Lenses, (c) Spreading Caused by Irregular Lenses

Source: Freeze and Cherry, 1979.

discontinuous high permeability layers have resulted in a greater mixing of the contaminant front. This tends to create a more homogeneous concentration pattern in the down gradient direction.

Most laboratory studies of dispersion have dealt with relatively homogeneous material, and the experimental results have generally indicated small dispersivity values. Experiments which have tried to approximate actual conditions have generally resulted in calculating values of dispersivity which are much larger than were calculated for homogeneous material. Numerical analyses of the effects of dispersion on contaminant transport (Pickens and Lennox, 1976) have indicated that large values of dispersivity cause more mixing of the contaminant than do smaller values of dispersion.

4. RELIABILITY OF PREDICTIVE METHODS

Many types of predictive methods are available which can be used to analyze the problem of groundwater contamination by organic chemicals. These methods range from simple analytical expressions for one-dimensional groundwater flow to multidimensional, multiphase, multicomponent reservoir simulation models. The simpler models are generally useful to a wider group of people and under a wider variety of circumstances than the more complex numerical simulation models. The more complex models can provide more detailed and precise answers to complex problems, but these advantages are frequently offset by the increased expenses related to data requirements and computer equipment, as well as the specialized training required for model application. The purpose of model application is to integrate several factors and to produce information on the basis of which intelligent decisions can be made. For the purpose of this project, these decisions are related to determining the source and/or extent of groundwater contamination, designing and executing the field data collection program to quantify the extent of contamination, and selecting the appropriate remedial action.

Classical approaches to problem solving have been to formulate the problem and then make as many simplifying assumptions as possible to produce a new problem which is manageable. For groundwater contamination problems, this may mean that a complex geometry is represented by a simpler geometry, that spatially or temporally varying properties are assumed to be constant, or that reacting chemical species are assumed to be nonreacting. The utility or reliability of the model results is dependent upon how well the simplified model represents actual conditions. When these conditions are closely approximated, then model results are directly applicable. Model results can also be useful when the limitations of model representations of actual conditions are known. The knowledge that the model results are not an accurate representation does not prevent use of the results to develop a better understanding of the system. Very few cases exist in nature where no answer is better than an approximate one, provided that the model limitations are known and understood.

Figure 88 illustrates how initial application of simplified models can aid the design of the field investigation program which, in turn, provides information which can be used to improve the model representation of the actual condition and lead to a better understanding of the physical system. The development of a better understanding of the physical environment and the simplified representation of this system leads to a better interpretation of model results and, makes the results more reliable.

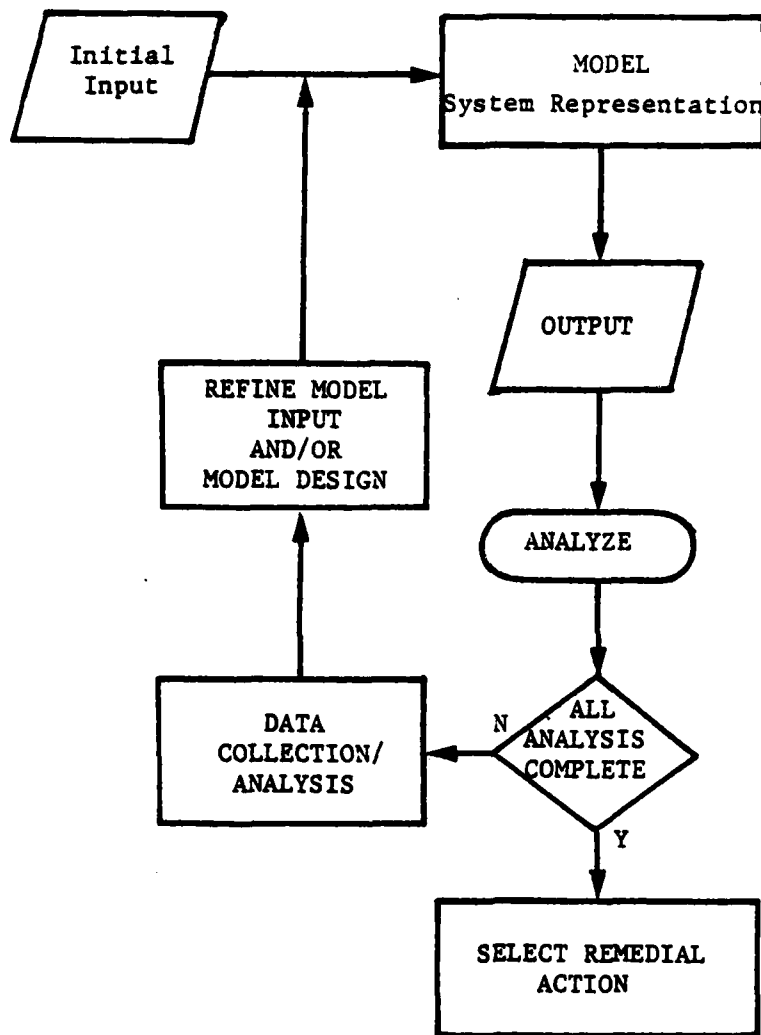


Figure 88. Schematic Representation of Interaction Between Model Analyses and Data Collection Program Leading to Selection of Remedial Action.

SECTION VI

GROUNDWATER TREATMENT CONTROL AND CONTAINMENT METHODS

1. GROUNDWATER TREATMENT METHODS

a. Introduction

Organic solvents, hydrocarbon fuels, pesticides, and other organics in groundwater present a number of issues for treatment selection. These compounds can usually be considered as members of one of the following chemical classes:

- alcohols
- ethers (halogenated)
- aliphatic hydrocarbons
- aromatics
- halocarbons
- pesticides
- phenols

Because alcohols are readily biodegradable, these compounds are not a major groundwater contamination problem. The other chemical classes are generally persistent in the environment and pose acute and/or chronic chemical toxicity hazards if ingested. Table 25 (from CEQ, 1981) summarizes the highest concentration level measured, and the results of carcinogenic testing of the 33 organic compounds most commonly found in drinking water wells.

Municipal drinking water wells typically yield 100 to 1,000 gallons per minute. A treatment facility to decontaminate groundwater would have to be capable of treating on the order of 100,000 to 1,000,000 gallons per day. The treatment capacity required could be increased by an order of magnitude if a major well field is contaminated.

b. Overview of Treatment Technologies

Groundwater contamination can be controlled by containment and treatment. Treatment is the focus of this section. Treatment technologies fall into one of the following classes:

- biological
- chemical
- physical

Biological processes uses microbes to metabolize the contaminants. Biological treatment methods include:

- activated sludge
- aerated surface impoundments
- trickling filters

TABLE 25. 33 ORGANIC COMPOUNDS MOST COMMONLY FOUND IN DRINKING
WELLS (CEQ 1981)

Chemical	Chemical Class	Highest Concentration (ppb)	Carcinogen Status*
Trichloroethylene	Halocarbons	27,300	CA
Toluene	Aromatics	6,400	NTA
1,1,1 Trichloroethane	Halocarbons	5,440	NA
Acetone	Ketone	3,000	
Methylene chloride	Halocarbons	3,000	NTA
Dioxane	Ether	2,100	CA
Ethyl benzene	Aromatic	2,000	
Tetrachloroethylene	Halocarbon	1,500	CA
Cyclohexane	Aliphatic Hydrocarbon	540	NTA
Chloroform	Halocarbons	490	CA
Di-n-butyl-phthalate	Phthalates		NTA
Carbon tetrachloride	Halocarbons	400	CA
Benzene	Aromatic	330	H
1,2-Dichloroethylene	Halocarbons	323	NTA
Ethylene dibromide	Halocarbons	300	CA
Xylene	Aromatics	300	NTA
Isopropyl benzene	Aromatics	290	NTA
1,1-Dichloroethylene	Halocarbons	280	NTA
1,2-Dichloroethane	Halocarbons	250	CA
Bis(2-ethylhexyl)phthalate	Phthalates	170	NTA
Dibromochloropropane	Pesticide	137	CA
Trifluorotrichloromethane	Halocarbons	135	NTA
Dibromochloromethane	Halocarbons	55	NTA
Vinyl Chloride	Halocarbons	50	H, CA
Chloromethane	Halocarbons	44	NTA
Butyl benzyl-phthalate	Phthalates	38	NTA
gamma-BHC(Lindane)	Pesticide	22	CA
1,1,2-Trichloroethane	Halocarbon	20	CA
Bromoform	Halocarbon	20	NTA
1,1-Dichloroethane	Halocarbon	7	SA
alpha-BHC	Pesticide	6	CA
Parathion	Pesticide	4.6	SA
delta-BHC	Pesticide	3.8	

* H = Confirmed human carcinogen
 CA = Confirmed animal carcinogen
 SA = Suggested animal carcinogen
 NA = Negative evidence of carcinogenicity from animal bioassay
 NTA = Not tested in animal bioassay
 Blank = No information found

- anerobic treatment
- land treatment

Activated sludge is the most commonly used biological process for wastewater treatment. Microbes oxidize or hydrolize organic compounds in an aerated tank. The activated sludge is separated in a clarifier and a portion is recycled to the aeration tank. Biological processes are capable of treating a wide range of organics but cannot effectively destroy refractory organics, such as PCBs, polynuclear aromatics, and halocarbons.

Chemical treatment destroys or immobilizes a contaminant by bringing it into contact with a chemical reactant. Chemical treatment methods include:

- alkaline chlorination (especially for cyanide)
- precipitation (primarily for selected inorganics, e.g., heavy metals)
- ion exchange
- chemical reduction (especially for chromium)
- ozonation
- wet air oxidation
- hydrolysis

The first four processes are applicable to inorganic contaminants rather than organic. Ozonation and wet air oxidation are the chemical methods most capable of destroying organic contaminants. Hydrolysis, especially when used with an accelerating catalyst, may be an important process for the destruction of some pesticides.

Physical treatment methods generally separate contaminants from waste streams based on such physical properties of the contaminant as density, molecular weight, solubility, etc. Physical treatment methods include:

- carbon adsorption
- stripping
- flotation
- sedimentation
- reverse osmosis

Carbon adsorption is applicable to a wide range of organic compounds which include organic solvents, hydrocarbons, and pesticides. Stripping and reverse osmosis may be applicable to some organic solvents and pesticides, respectively.

The applicability of treatment methods to the chemical classes cited herein is summarized in Table 26.

Application of treatment technologies to groundwater contamination problems has been limited. In a survey of 169 uncontrolled hazardous

TABLE 26. TREATMENT PROCESS APPLICABILITY MATRIX
(USEPA 1980c)

TREATMENT TECHNOLOGY	Alcohols	Aliphatics	Aromatics	Ethers	Halocarbons	Pesticides	Phenols	Phthalates
Biological Treatment								
Activated Sludge	E	V	V	G	F	H,F	G	G
Rotating Biological Disc	E	V	V	G	F	H,F	G	G
Trickling Filter	E	V	V	G	F	H,F	G	G
Surface Impoundment	E	V	V	G	F	H,F	G	G
Land Treatment	E	V	V	G	F	H,F	G	G
Chemical Treatment								
Alkaline Chlorination	N	N	N	N	N	X	N	N
Ozonation	G,E	F	F,G		F,G	E	E	
Chemical Reduction	N	N	N	N	N	N	N	N
Precipitation			F					G
Ion Exchange								
Wet Air Oxidation	X	X	X	X	X	X	X	X
Physical Treatment								
Carbon Adsorption	V	V	G,E	V	G,E	E	E	E
Sedimentation								
Flotation								
Filtration								
Reverse Osmosis	V	V	V			E	V	
Stripping								

Key

- E = Excellent Performance Likely
- G = Good Performance Likely
- F = Fair Performance Likely
- P = Poor Performance Likely
- N = Not Applicable
- V = Variable Performance Reported for Different Compounds in the Class
- X = Treatment is Applicable but not Specified in the Source Reference
- A Blank Indicates No Data Available

waste sites, groundwater leachate was reported to have been contaminated at 110 sites (65 percent of the sites) (Neely, N. et al., 1981). The survey results revealed some form of treatment had been undertaken* at only 24 sites (~ 1/5 of those reporting groundwater contamination).

The treatment technologies reported as being used (or proposed for use) were as follows:

<u>Treatment Technology</u>	<u>No. of Sites Using Technology</u>
Activated carbon or charcoal	8
Leachate recirculation through soil/landfill or process	4
Aeration†	4
Chemical treatment for removal of inorganics (e.g., precipitation, oxidation)	2
Biostimulation	1
Unspecified treatment method	5
	<u>24</u>

† Aeration is discussed under Activated Sludge Treatment in the next subsection.

c. Process Treatment Trains

Contaminated groundwater generally contains a mixture of contaminants, all of which can seldom be successfully treated by one technology. Therefore, it is usually necessary to employ more than one technology. Based on laboratory results, effective treatment methods and a sequential process treatment can be chosen. Data requirements necessary to select a process treatment train are summarized in Table 27. An example process treatment train to treat an aqueous mixture of metal salts and chlorinated solvents is shown in Figure 89. A detailed analysis of process treatment train selection can be found in USEPA 1980c.

d. Treatment Technologies

This subsection contains a detailed discussion of technologies which are applicable to organic contaminants in groundwater. These technologies are (USEPA 1981c):

* "Treatment" not considered to include diversion, isolation, simple pumping, or purging.

TABLE 27. DATA REQUIREMENTS TO SELECT TREATMENT PROCESS

TREATMENT TECHNOLOGY	Volume	TKN	Flow	pH	Acidity Expressed as CaCO_3 Equivalent	BOD	COD	TOC	TSS	TDS	Metals	Cyanide	Temperature	Complexing Agents	Viscosity	Climate	Soil Permeability	Soil CEC	Oxidation Reduction Potential	Leachate Variability	Phosphorus Content	Particle Size of Suspended Solids	Presence of Interfering Species
Biological Treatment																							
Activated Sludge	X	X	X	X	X	X	X	X	X		X	X	X	X			X				X		X
Rotating Biological Dis	X	X	X	X	X	X	X	X	X		X	X	X	X			X				X		X
Trickling Filter	X	X	X	X	X	X	X	X	X		X	X	X	X			X				X		X
Surface Impoundment	X	X	X	X	X	X	X	X	X		X	X	X	X			X				X		X
Land Treatment	X	X	X	X	X	X	X	X	X		X	X	X	X			X	X			X		X
Chemical Treatment																							
Alkaline Chlorination	X		X	X	X																		
Ozonation	X		X	X	X																		
Chemical Reduction	X		X	X	X																		
Precipitation	X		X	X	X																		
Ion Exchange	X		X	X	X																		
Wet Air Oxidation	X		X	X	X			X															
Physical Treatment																							
Carbon Adsorption	X		X	X			X	X		X					X								
Sedimentation	X		X	X																			
Flotation	X		X	X																			
Filtration	X		X	X																			
Reverse Osmosis	X		X	X																			
Stripping	X		X	X																			

Source: ADL, 1982

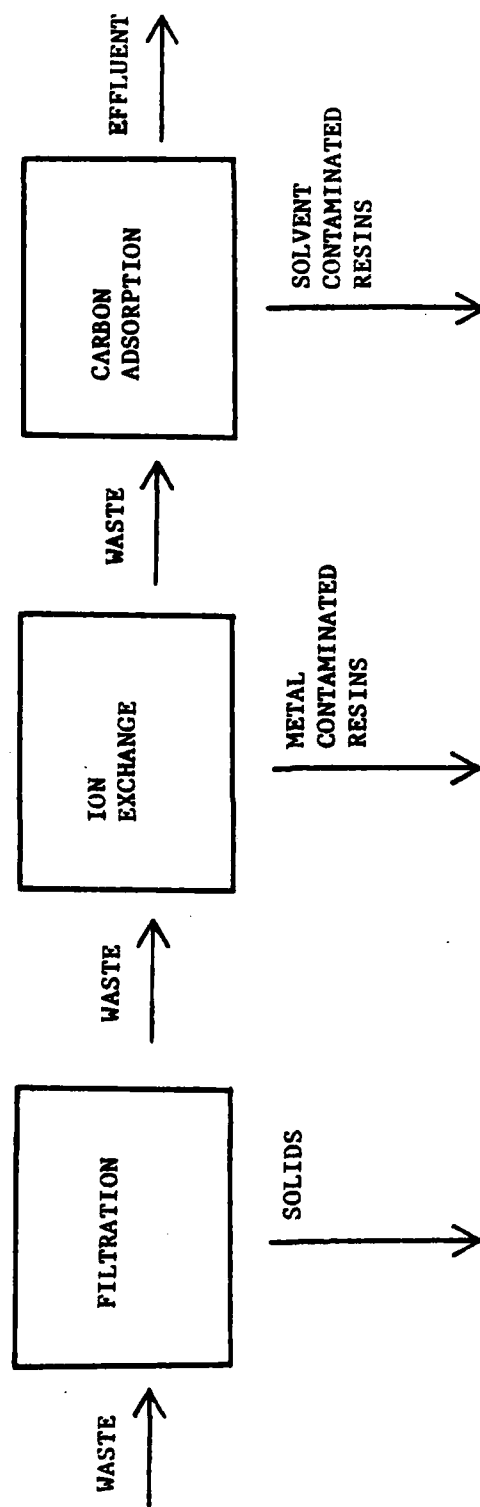


Figure 89. Process Treatment Train For An Aqueous Mixture Of Metals and Chlorinated Solvents

- activated sludge
- carbon adsorption
- ozonation/UV
- stripping
- reverse osmosis/wet air oxidation

Selection of these technologies was based on the availability, experience, and range of applicability of the technology. Activated sludge is not usually an effective method to destroy halogenated solvents but was included because activated sludge sewage treatment systems are available at many military bases and would certainly be considered as a treatment option. Reverse osmosis is considered in combination with wet air oxidation as a potential method to concentrate and subsequently destroy pesticides. The remaining technologies are generally suitable for the removal or destruction of organic solvents and/or pesticides.

Technology discussions will all follow the same format and address:

- Technology Description
- Operating Characteristics
- Design Considerations

(1) Activated Sludge

(a) Description

Bacteria are utilized by the activated sludge process to oxidize and hydrolize organic waste in aqueous waste streams. The bacteria become acclimated to the wastewater environment through continuous recycle as shown in Figure 90.

The process includes an aeration basin, a clarifier, and equipment to recycle a portion of the activated sludge from the clarifier to the aeration basin. An aeration system releases either air or pure oxygen into the aeration tanks. Aeration methods are summarized in Table 28. Equalization, neutralization, and/or primary sedimentation may precede activated sludge processing. Activated sludge treatment yields a treated effluent and a residual sludge. Sludge disposal options include landfill, incineration, and composting.

(b) Operation Characteristics

Performance criteria for activated sludge processing systems are usually based on BOD removal efficiency. Mean BOD removal efficiency for 92 industrial wastewater streams, which were studied by the USEPA, was 86 percent (USEPA, 1980d). Mean influent and effluent levels were 1310 and 184 mg/l respectively. In contaminated groundwater treatment applications, removal efficiencies for specific compounds may be a much more important measure of the technology effectiveness. Activated sludge is not very effective for removal of halogenated solvents or pesticides from aqueous streams. For example, for five industrial

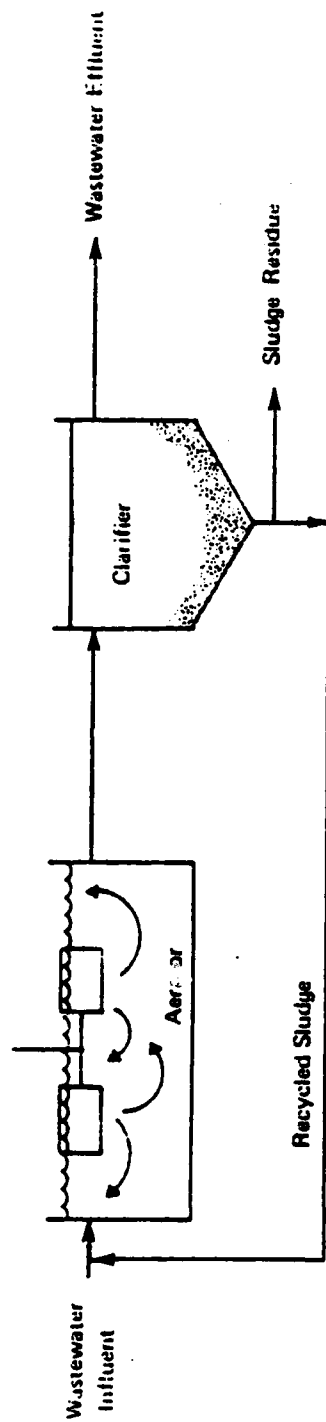


Figure 90. Typical Activated Sludge

Source: ADL, 1976

TABLE 28. SUMMARY OF AERATION METHODS

Method	Description	Application
Extended Aeration	Longer wastewater retention times in the aeration basin.	Low organic loading and reduced sludge quantities desired.
Pure Oxygen Aeration	Wastewater aeration with pure oxygen in a closed aeration tank.	High organic and/or metal loading.
Contact Stabilization	Aeration of recycled sludge on its return to the aeration tank.	Sludge removes BOD rapidly by biosorption. Contact stabilization decomposes the sorbed organics.

Source: ADL, 1976

wastewater streams containing a 26 mg/l mean concentration of methylene chloride studied by the USEPA, removal efficiency was only 34 percent (USEPA 1980d). Removal was probably due to volatilization of the methylene chloride rather than biodegradation.

Effective operation of activated sludge systems requires that the influent pH level be near neutral and the process loading be constant. A pH adjustment system and an equalization tank are pretreatment processes usually employed to ensure an acceptable influent for activated sludge processing. If toxic species, such as heavy metal ions exist, then pretreatment may be required to remove them. Threshold toxicity concentrations for some metals are summarized in Table 29.

(c) Design Considerations

The major design factors are (Adams & Eckenfelder, 1974):

- retention time
- oxygen requirements
- food to microorganism ratio
- nutrient requirements
- sludge production

Based on these factors, the aeration tank(s) and clarifier can be sized, horsepower requirements for the aeration system determined, quantities of phosphorous and nitrogen needed to satisfy nutrient requirements determined, and sludge disposal needs defined. Design equations can be found in Adams and Eckenfelder (1974).

To generate quantitative design information, the following site specific information is necessary (Adams and Eckenfelder, 1974):

- biodegradable sludge fraction
- total Kjeldahl nitrogen in influent (TKN)
- total phosphorous concentration in influent
- BOD or specific contaminant removal rate
- oxygen requirements
- sludge generation rate
- presence of interfering pollutants in influent

The last four information requirements listed are best determined by treatability studies. Removal rates are typically temperature dependent and should be studied over the expected operating temperatures at the site.

(2) Carbon Adsorption

(a) Technology Description

Carbon adsorption removes contaminants from an aqueous waste stream by binding the contaminants to the surface of a solid, activated carbon adsorbent. The carbon adsorbent is generally in a granular form, but a

TABLE 29. POTW THRESHOLD INTERFERENCE LEVELS* OF SOME AQUEOUS CONTAMINANTS

Contaminant	Threshold Concentration (mg/l)	
	Chronic	+Slug Dose
Cyanide	1 ¹	40 ¹
Copper	1 ²	75 ²
Nickel	1-2.5 ²	50-200 ²
Zinc	5-10 ²	160 ²
Chromium	10 ²	>500 ²
Lead	*1 ¹	-
Cadmium	-	0.5 ³
Silver	5 ²³	-

*Threshold level: 2-10% increase in BOD or COD of waste water effluent

+Slug dose: 4-hour exposure which causes a significant impact on the POTW for a 24-hour period

¹Federal Guidelines: State and Local Pretreatment Programs, Vol. 1, EPA-430/9-76-017a, p. E1-E26, 1977.

²Barth, E.F., et al, "Summary Report on the Effects of Heavy Metals on the Biological Treatment Process," J. WPCF, Vol. 37, p. 86, 1965.

³Cenci, G., et al, "Evaluation of the toxic effect of Cd⁺² and Cd(Cn)₄⁻² on the growth of mixed microbial population of activated sludges," The Science of the Total Environment 7 p. 131-143, 1977.

Source: Arthur D. Little, Inc., 1982.

powdered form is also used. Several operating configurations for granular activated carbon systems are shown in Figure 91. Carbon adsorption is capable of removing a wide range of organic compounds and some inorganic species such as: antimony, arsenic, chromium, mercury, and silver (USEPA, 1982b). A treated effluent and a contaminated carbon are the products of carbon adsorption treatment. The contaminated carbon can either be disposed of by landfilling or incineration, or reactivated by thermal methods.

(b) Operating Characteristics

Carbon adsorption is typically used to remove organic compounds which are not treatable by biological methods. Organics can be reduced to very low concentration levels with a well-designed and well-operated system. Carbon adsorption is most applicable to nonpolar, high molecular weight, slightly soluble organics (USEPA 1980d). Results of an EPA study indicated that 51 of the 60 toxic organic compounds tested could be removed by carbon adsorption. For further discussion on operating characteristics of carbon adsorption systems see: Symons, 1978; EPA, 1978a; Symons, 1979; Symons, 1980; Wood, 1978; and Demarco, 1978.

Several carbon adsorption contacting methods are used (see Figure 91). In granular activated carbon systems, the aqueous stream contacts the carbon as it flows through a fixed or moving bed. As the carbon adsorption capacity becomes spent, it is replaced with new or regenerated carbon. In powdered carbon systems, finely ground carbon is mixed with the aqueous stream and after sufficient contact time is removed and generally disposed. A typical mode of operation is to add the powdered carbon to the clarifier of an activated sludge system. Contacting methods and corresponding application conditions are summarized in Table 30.

Effective operation requires a fairly uniform influent. Because a system is sensitive to changes in the influent character, systems are generally oversized to prevent contaminant breakthrough in the case of increased flow rates and/or higher influent contaminant levels. If influent quantity or character vary widely, an equalization tank should precede the carbon adsorption system. Influent levels of suspended solids, and oil and grease greater than 50 ppm and 10 ppm, respectively, interfere with granular carbon adsorption systems (ADL, 1976). Biological activity sometimes occurs in the carbon system and can contribute positively via biodegradation or negatively via clogging.

(c) Design Considerations

The major design factors are:

- carbon system contacting configuration
- type of activated carbon
- carbon usage rate
- carbon regeneration carbon

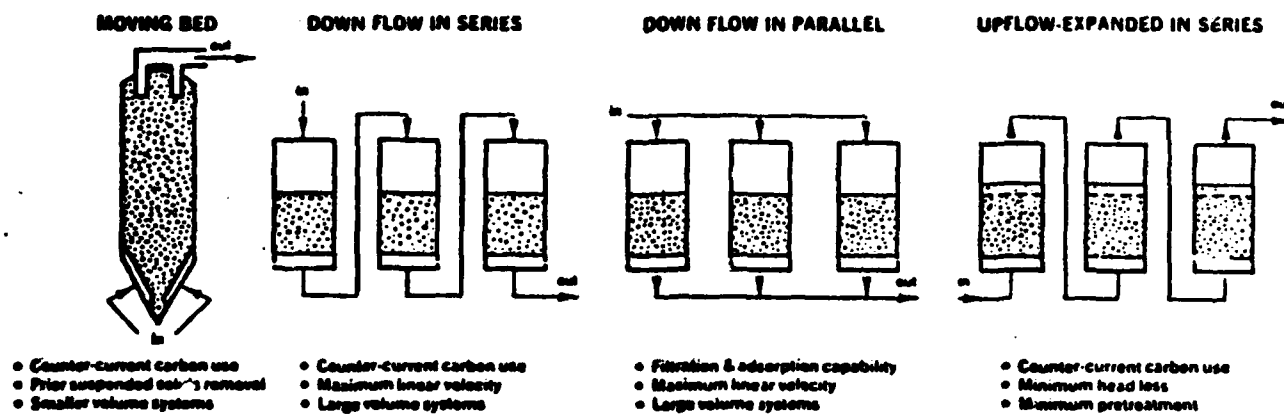


Figure 91. Granular Activated Carbon System Configuration

Source; ADL, 1976

TABLE 30. CONTACTING SYSTEMS

Method	Application Conditions	Comments
Single or parallel	<ul style="list-style-type: none"> • Pollutant breakthrough curve is steep. • Carbon recharge interval is long. • Volume flow is high. • Influent is viscous. 	<ul style="list-style-type: none"> • Typical flows are 1 to 4 gpm/ft². • Parallel system is usually selected if pressure drop problems are expected for the system. • Moderate adsorbent expense.
Adsorbers in series	<ul style="list-style-type: none"> • Pollutant breakthrough curve is gradual. • Uninterrupted operation is necessary. • Relatively low effluent concentration is required. • Carbon recharge interval is short. 	<ul style="list-style-type: none"> • Typical flows are 3-7 gpm/ft². • High adsorbent expense.
Expanded upflow adsorber(s)	<ul style="list-style-type: none"> • For high flows and high suspended solids concentrations. 	<ul style="list-style-type: none"> • Typical flows are 5-9 gpm/ft². • Suspended solids are passed through the column and not separated.
Moving bed	<ul style="list-style-type: none"> • For systems requiring efficient use of carbon (i.e., carbon adsorption capacity is exhausted before removal from column). 	<ul style="list-style-type: none"> • Influent must contain less than 10 mg/l TSS, and not biologically active. Either parameter will cause a pressure drop in the system and necessitate removal of carbon prior exhaustion of its adsorption capacity.
Powdered carbon with subsequent clarifier and/or filter	<ul style="list-style-type: none"> • Carbon usage higher than for series of fixed-bed adsorbers. • Influent concentration of pollutants should be relatively constant to avoid frequent sampling and adjustment of carbon dosage. 	<ul style="list-style-type: none"> • No restrictions on suspended solids or oil and grease in influent. • Capital equipment costs relatively low. • Simple to operate.
Powdered activated carbon with activated sludge	<ul style="list-style-type: none"> • For activated sludge systems receiving toxic or shock organic loadings. 	<ul style="list-style-type: none"> • Protects the biological system from toxic organics and shock loadings. Generally improves effluent quality.

Source: ADH, 1976

The contacting configuration is based on the application conditions summarized in Table 30.

Carbon selection is an important consideration for optimizing the treatment process for the specific aqueous stream. Laboratory testing is required to determine the appropriate carbon for each specific waste stream. Properties of several commercially available carbons are summarized in Table 31. The general laboratory test procedure is to mix different quantities of activated carbon with batches of the contaminated aqueous stream and analyze the equilibrium conditions to generate adsorption isotherms. Based on the adsorption isotherms, a carbon type is selected. For a more detailed discussion of carbon adsorption isotherms, see Schweitzer (1979) or Adam and Eckenfelder (1974).

Because carbon usage cannot be determined by the carbon adsorption isotherm results, laboratory testing a flow-through system is required to size a system. A common test method used is known as the bed-depth/service time analysis (BDST) (Adams and Eckenfelder, 1974). Three to four columns are connected in series under hydraulic loads which simulate field conditions. Effluent from each column is analyzed for the chemicals of concern. The effluent-to-influent ratio for the chemicals measured is plotted against the total bed-depth. Based on these results and the carbon contacting system to be used, the carbon usage can be calculated. For more details on BDST analysis and carbon usage calculations, see Adams and Eckenfelder (1974).

Carbon regeneration rates for industrial waste carbon treatment systems in a multiple hearth furnace are approximately 3.5 lb/hr-ft² (Adams and Eckenfelder, 1974). Generally, a carbon usage rate of 1,000 pounds per day is considered the cutoff point for economic regeneration versus disposal.

The following site-specific data are required to design a carbon adsorption system:

- influent contaminant levels
- influent flow rate
- presence of interfering contaminants in influent
- carbon adsorption isotherms
- bed-depth/service time analysis

(3) Ozonation/Ultraviolet

(a) Technology Description

Ozone (O₃) is produced in a generator (ozonator) and introduced into a contacting chamber where it oxidizes a wide range of contaminants. Ozone is a strong oxidizing agent capable of oxidizing many refractory organic compounds in the following chemical classes:

TABLE 31. PROPERTIES OF SEVERAL COMMERCIALY AVAILABLE CARBONS*

PHYSICAL PROPERTIES	ICI AMERICA HYDRODARCO 3000	CALGON FILTRASORB 300 (8x30)	WESTVACO NUCHAR WV-L (8x30)	WITCO 517 (12x30)
Surface area, m ² /gm (BET)	600-650	950-1050	1000	1050
Apparent density, gm/cc	0.43	0.48	0.48	0.48
Density, backwashed and drained, lb/cu ft	22	26	26	30
Real density, gm/cc	2.0	2.1	2.1	2.1
Particle density, gm/cc	1.4-1.5	1.3-1.4	1.4	0.92
Effective size, mm	0.8-0.9	0.8-0.9	0.85-1.05	0.89
Uniformity coefficient	1.7	1.9 or less	1.8 or less	1.44
Pore volume, cc/gm	0.95	0.85	0.85	0.80
Mean particle diameter, mm	1.6	1.5-1.7	1.5-1.7	1.2
SPECIFICATIONS				
Sieve size (U.S. std. series)				
Larger than No. 8 (max. %)	8	8	8	-
Larger than No. 12 (max. %)	-	-	-	5
Smaller than No. 30 (max. %)	5	5	5	5
Smaller than No. 40 (max. %)	-	-	-	-
Iodine No.	650	900	950	1000
Abrasion No., minimum	**	70	70	85
Ash (%)	**	8	7.5	0.5
Moisture as packed (max. %)	**	2	2	1

* Other sizes of carbon are available on request from the manufacturers.

** No available data from the manufacturer.

- Not applicable to this size carbon.

Source: ADL, 1976

- chlorinated hydrocarbons
- chlorinated aromatics
- pesticides

The oxidation of refractory organic compounds is improved by combining ultraviolet light with ozonation as shown in Figure 92. Because ozone is acutely toxic, systems are equipped with automated devices which measure ozone levels in the gaseous effluent and reduce the ozonator voltage and frequency if gaseous levels exceed a preset limit (generally 0.05 ppm). These systems are also equipped with air monitors which sound an alarm and shut off the ozonator if an ozone leak occurs.

(b) Operating Characteristics

Ozonation is typically used to treat waste streams containing less than 1 percent oxidizable material. Because ozone is not a selective oxidizer, the presence of oxidizable materials other than target pollutants will increase the cost of the treatment. A list of organics which are economically treatable by O_3 /UV is presented in Table 32.

Ozonators produce low concentrations of ozone in air (less than 2 percent). The contact chambers are large (typical depths of 5 meters) because reaction rates are limited by mass transfer. Ultraviolet lamps, when utilized, are operated in the contactor chamber. Typical UV operating power levels range from 1 to 10 watts per liter (Prengle, 1975).

Because ozone is corrosive, ozonation equipment requires special construction materials which include:

- stainless steel
- unplasticized PVC
- aluminum
- teflon
- chromium plated brass or bronze

(c) Design Considerations

Key design factors are:

- ozone dose rate
- retention time
- ultraviolet light dosage

Ozone dose rate is expressed as either ppm ozone or pounds of ozone per pound of aqueous constituents oxidized. Dose rates usually range from 10 to 40 ppm for the former and 1.5 to 3.0 pounds per pound of contaminants oxidized for the latter (ADL, 1976). Dosage rates are usually set based on laboratory studies.

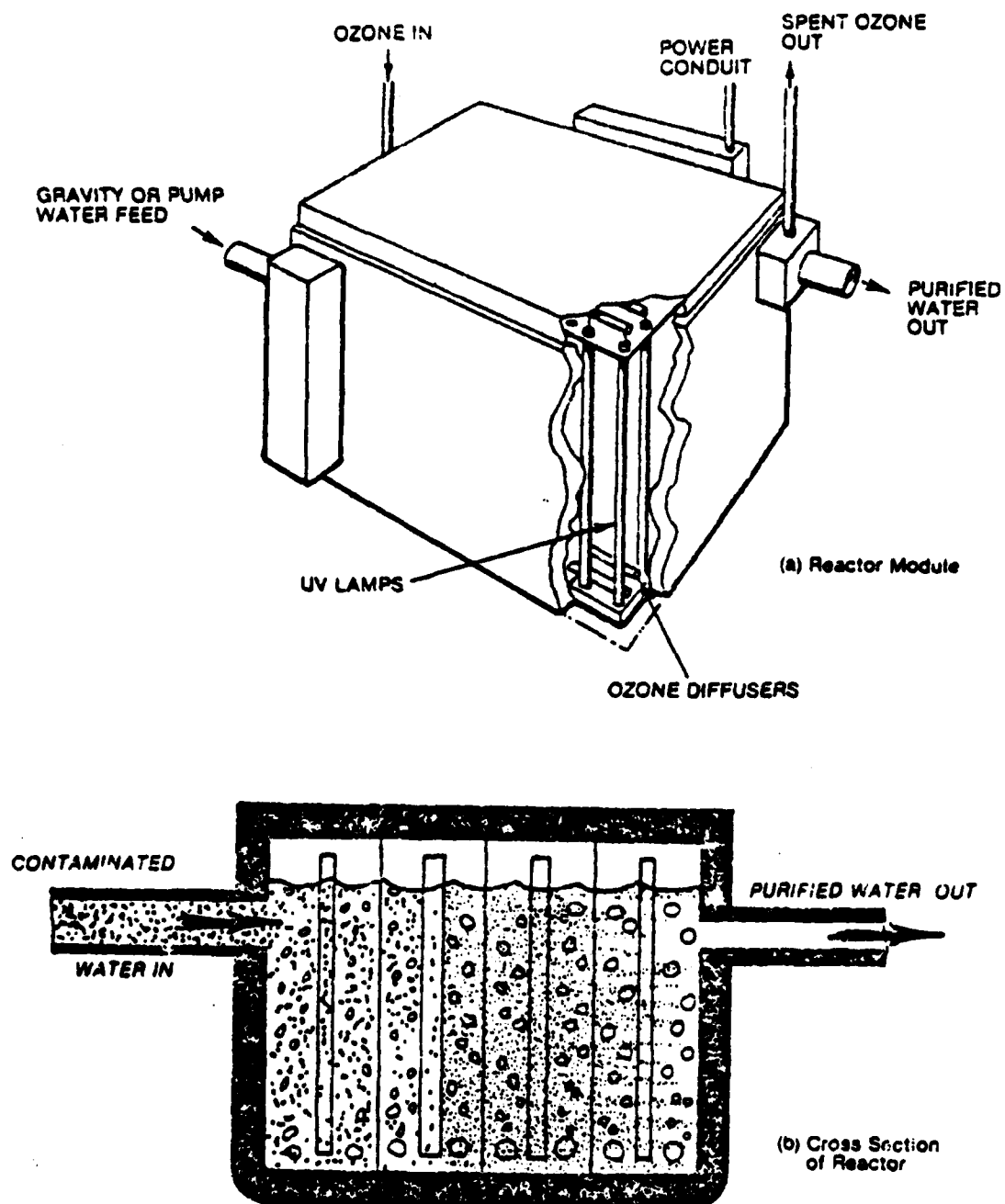


Figure 92. Schematics of an O_3/UV Reactor

Source: Ghassemi, 1981

TABLE 32. LIST OF ORGANICS DETERMINED TO BE ECONOMICALLY
TREATABLE BY THE O₃/UV PROCESS

Acetaldehyde	Glycols
Acetic acid	Hydroquinone
Alcohols	Kepone
Aldrin	Methylene chloride
Amines	Nitrobenzene
Anisole	Nitrophenol
Benzoic acid	Organic phosphates
Chelating compounds	Organosulfur compounds
Chlorinated phenols	Organo-tin compounds
Chlorobenzene	PCB's
Detergents	Phenol
Dieldrin	Phthalic acid
Diethylphthalate	RDX
Endrin	Sodium acetate
Ethylene dichloride	Styrene
Formaldehyde	Sugars
Formic acid	TNT
Glycerols	Vinyl chloride
Glycine	Xylenol

Source: Ghassemi, 1981

Retention times generally range from 10 minutes to one hour in a multistage application. The design parameter is generally set based on laboratory studies. If ultraviolet light is used, the dose rate is also determined by laboratory studies.

Data requirements for system design include:

- treatment stream flow rate
- concentration of oxidizable constituents
- ozone dosage
- retention time
- ultraviolet light dosage
- operating temperature

(4) Stripping

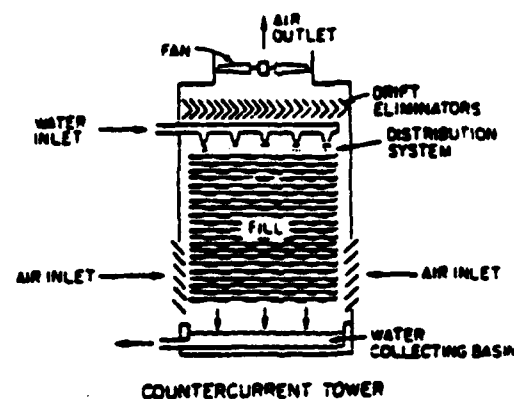
(a) Technology Description

Stripping removes volatile components from an aqueous waste stream by passing air or steam through the waste stream. The "stripped" constituents must be removed from the gas stream by subsequent treatment, such as carbon adsorption or condensation. Stripping has been mainly used to remove ammonia from water, but is applicable to volatile organics (Kelleher, 1981; Shuckrow *et al.*, 1981). Figures 93 and 94 show typical air and steam stripping process designs.

(b) Operating Characteristics

Air stripping is capable of achieving ammonia removal efficiencies of greater than 90 percent for aqueous streams containing less than 100 ppm (ADL, 1976). An EPA study (USEPA 1980d) reported that steam stripping removal efficiencies for volatile organics range from 10 to 97 percent. For example, the average removal efficiencies for chloroform and 1,1,2,2-tetrachloroethane were 89 percent and 40 percent. These results represent 5 data points for each pollutant. The average influent concentration was 65,000 ug/l and 78,000 ug/l for chloroform and 1,1,2,2-tetrachloroethane. Application of air stripping to remove 1,1,1-trichloroethane (TCEA) from a contaminated groundwater drinking supply resulted in the reduction of TCEA concentrations from 1200 ppb to 10 ppb (Kelleher, 1981). Other studies also indicate that air stripping is suitable for removing volatile organic compounds (Shuckrow, 1981; James, 1981). Laboratory studies of removal efficiencies for a particular organic constituent are necessary because removal efficiencies are dependent on the characteristics of each aqueous stream (Gosset, 1981).

In an air stripping process, wastewater flows counter current to an air stream. For ammonia removal, the influent pH is maintained in the 11-12 range. Typical operating parameter values for ammonia stripping are 40 L/(min-m²) hydraulic load and a 400 ft³/gal air flow rate (ADL, 1976).



Source: USEPA 1982b

Figure 93. Air Stripping Tower

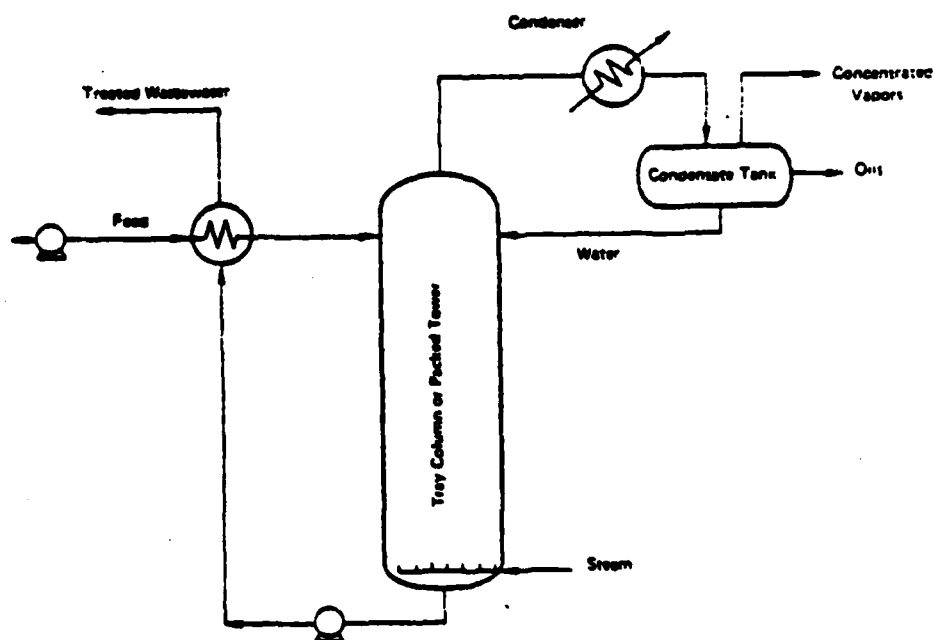


Figure 94. Typical Steam Stripping System

Source: ADL, 1976

In a steam stripping operation, the wastewater is typically introduced at the top of a distillation column and steam at the bottom. The steam and stripped wastewater components flow through a condenser. Condensed water is recycled and the pollutants are collected. Typical operating conditions are 0.6-2.0 pounds of steam per gallon of water treated and a wastewater flow of 200 gallons per minute.

(c) Design Considerations

For air stripping, the hydraulic load, air flow, depth of stripping tower, operating temperature and aqueous stream pH (if NH_3 is the stripping target) are important design factors (ADL, 1976). For steam stripping, the treatment stream flow, steam flow, and column size are also important design factors (USEPA 1980d).

Information required to design a stripping system includes (Adams and Eckenfelder, 1978):

- aqueous treatment stream flow
- water temperature
- cold weather wet bulb temperature
- pH (for ammonia)
- influent concentration

(5) Reverse Osmosis/Wet Air Oxidation

(a) Technology Description

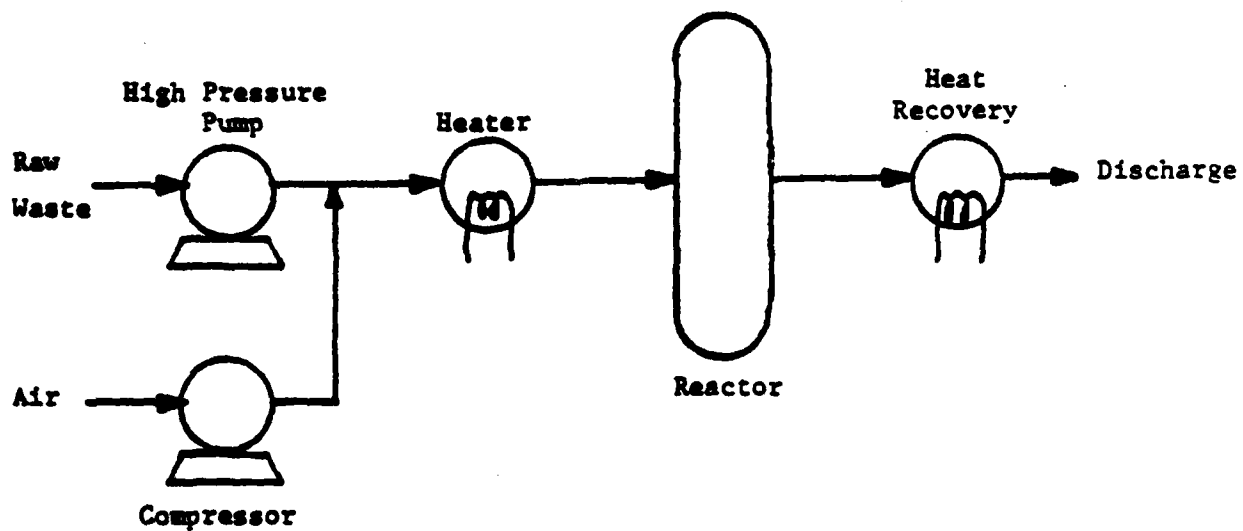
Reverse osmosis separates contaminants from wastewater by forcing water through a membrane which is impermeable to most soluble inorganic species and some organic compounds. Wet air oxidation is a thermal oxidation process which oxidizes waste in the liquid phase at high pressure and high temperature. A wet air oxidation process schematic is shown in Figure 95. These two technologies are considered together because, used in consort, they could be effective for treating groundwater contaminated with high molecular weight organic compounds (300-500 g/mol). Reverse osmosis would be utilized to concentrate the organic constituents followed by wet air oxidation of the concentrate.

(b) Operating Characteristics

Reverse osmosis systems are typically operated in the 200-400 psi range. The operating characteristics of the three basic reverse osmosis module configurations are summarized in Table 33.

Reverse osmosis removal efficiencies are species and waste stream specific. An EPA study (USEPA 1980d) reported on average TOC removal efficiency of 84 percent for 18 data points.

Wet air oxidation is typically applied to waste streams containing 1 to 15 percent organic material. These concentrations are too high for conventional biological treatment or carbon adsorption, and generally



After: Ghassemi, 1981

Figure 95. Schematic of Wet Air Oxidation

TABLE 33. COMPARISON OF REVERSE OSMOSIS MODULE CONFIGURATION

	Spiral wrap	Tubular	Hollow fine fiber
Membrane surface area per volume, ft ² /ft ³	100 - 300	40 - 100	5,000 - 10,000
Product water flux, gpd/ft ²	8 - 25†	8 - 25	0.1 - 2
Typical module factors:			
Brine velocity, ft/sec	‡	1.5	0.04
Brine channel diameter, in	0.03‡	0.5	0.004
Method of membrane replacement	As a membrane module assembly - on site	As tubes - on site	As entire pressure module - on site, module returned to factory
Membrane replacement labor	Low	High	Medium - requires equipment
High pressure limitation	Membrane compaction	Membrane compaction	Fiber collapse
Pressure drop, product water side	Medium	Low	High
Pressure drop, feed to brine exit	Medium	High	Low
Concentration polarization problem	Medium	High	High
Membrane cleaning - mechanical	No	Yes	No
- chemical	Yes - pH and solvent limited	Yes - pH and solvent limited	Yes - less restricted
Particulate in feed	Some filtration required	No problem	Filtration required

†Product flux varies with the net driving pressure and temperature; a flux of 10-25 gpd/ft² is typical at a pressure of about 400 psi.

‡It is difficult to define velocity in a spiral element since the space between membrane is filled with a polypropylene screen which acts as a spacer and turbulent promoter.

§Height of brine channel (not diameter).

**Permissible pH and temperature ranges dependent primarily on membrane type and not on module configuration; for example, polyamide hollow fine fiber is pH limited from 4 to 11, cellulose acetate from 3 to 7.5, thin film composite (TFC) spirals have been operated and cleaned at pH levels ranging from 1 to 12.

Source: Ghassemi, 1981

too low for cost-effective incineration. A summary of destruction efficiencies for ten priority pollutants is presented in Table 34. Units are typically operated at pressures of 24 atmospheres and temperatures of 300 degrees centigrade.

The effective utilization of reverse osmosis and wet air oxidation to remove and destroy organic compounds is limited by the concentration of inorganic salts in the groundwater. If the inorganic salt concentration is too high in relation to the organic concentration, then reverse osmosis treatment will not be capable of producing a sufficiently concentrated solution for economical destruction by wet air oxidation.

(c) Design Considerations

Flow, solvent flux, and solute flux are key design considerations for designing a reverse osmosis treatment system. For a discussion on calculating solvent flux and solute flux, see Ghassemi (1981). Reactor pressure, operating temperature, and retention time are key design considerations for wet air oxidation. A more detailed discussion of these design parameters can be found in Ghassemi, 1981.

Information required to design a reverse osmosis system includes:

- solvent flux
- solute flux
- hydraulic load
- total dissolved solvents in influent
- influent pH
- operating temperature

Information required to design a wet air oxidation system includes:

- treatment flow rate
- concentration of oxidizable materials
- laboratory studies to determine optimum operating pressure and temperature

2. GROUNDWATER CONTROL AND CONTAINMENT METHODS

a. Introduction

In certain circumstances, groundwater contamination can be effectively controlled by containing, rather than treating, the source of contamination or the contaminated plume. The purpose of leachate treatment methods is to remove the hazardous constituents from groundwater after it has been removed from the ground. Control and containment methods, on the other hand, are designed to prevent hazardous constituents from entering groundwater or to restrict the movements of contaminated groundwater. In some cases, both treatment and containment may be appropriate.

TABLE 34. WAO EFFICIENCY FOR TEN PRIORITY POLLUTANTS
(1-HOUR DETENTION TIMES)

Compound	Starting concentration (g/l)	% Starting material destroyed	
		320°C	275°C
Acenaphthene	7.0	99.96	99.99
Acrolein	8.41	>99.96*	99.05
Acrylonitrile	8.06	99.91	99.00†
2-Chlorophenol	12.41	99.86	94.96†
2,4-Dimethylphenol	8.22	99.99	99.99
2,4-Dinitrotoluene	10.0	99.88	99.74
1,2-Diphenylhydrazine	5.0	99.98	00.08
4-Nitrophenol	10.0	99.96	99.60
Pentachlorophenol	5.0	99.88	81.96†
Phenol	10.0	99.97	99.77

* The concentration remaining was less than the detection limit of 3 mg/l.

† The percent destruction from acrylonitrile, 2-chlorophenol, and pentachlorophenol at 275°C was increased to 99.50, 99.88, and 97.3 by addition of cupric sulfate (catalyst).

Source: Ghassemi, 1981

Groundwater control and containment measures are not limited to methods which act on the groundwater alone. The entire water balance at the site, as well as the location of the source of contamination with respect to the water table, must be considered. Cutting off groundwater flow upgradient of a site, for example, would be ineffective where the source of contamination is above the water table, where infiltration of surface water through the source is a problem, or where the source contains liquid wastes. These require other source control measures, such as surface water control methods or excavation. Upgradient groundwater control, however, would be appropriate if groundwater flow through the source is the primary means of release of hazardous constituents into the groundwater. The types of control and containment measures which will be most effective should be determined on a site-by-site basis. Data requirements for evaluating groundwater control and containment technologies are summarized in Table 35.

b. Control and Containment Technologies

This subsection contains a detailed discussion of technologies applicable to the control and containment of contaminated groundwater. Categories of technologies discussed are:

- Impermeable Barriers
- Groundwater Pumping
- Leachate Collection
- Removal
- Surface Water Control

Discussions include a description of the technologies in the category and engineering (design) information necessary to determine a technology's applicability at a given site.

(1) . Impermeable Barriers

(a) Description

Impermeable barriers are underground physical barriers designed to restrict groundwater flow. The most common impermeable (actually low permeability) barriers in use today are slurry walls, grout curtains, and sheet piles.

Slurry walls are constructed by digging a trench using a soil or cement bentonite and water mixture (slurry) to maintain the trench during excavation. For soil-bentonite (SB) slurry walls, the trench is then backfilled with carefully engineered, low-permeability soil. For cement-bentonite (CB) slurry walls, the slurry sets to form a low permeability barrier. Effectiveness of the slurry wall depends both on the characteristics of the SB backfill or set CB slurry, as well as on the formation of a slurry filter cake on the sides of the trench during construction.

TABLE 35. GROUNDWATER CONTROL AND CONTAINMENT TECHNOLOGY DATA REQUIREMENTS

Technology	soil										groundwater												
	Topography	Site of Material Accessibility	Vegetation	Depth to Impermeable Stratum	Soil Type	Grain Size Distribution	Compaction	Moisture Content	Permeability	Porosity	Depth	Chemistry	Climatic Conditions	Depth to Water Table	Potentiometric Surfaces	Direction/Rate of Flow	Recharge	Aquifer Characteristics	Chemistry	Infiltration	Runoff	Drainage Area	Waste Characteristics
x useful data	/	x	x	x	x	x	x	x	x	x	x	x	x	/	/	/	/	x	x	x	/		/
/ primary data required	/	/		/	/	/	/	/	/	/	/	/		/	/	/	/	/	/	/	/	/	/
Slurry Walls	x	/		/	/	/	/	/	/	/	/	/		/	/	/	/	/	/	/	/	/	/
Grout Curtains	x	/		/	/	/	/	/	/	/	/	/		/	/	/	/	/	/	/	/	/	/
Sheet Piles	x	x		/	/	/	/		x	x	x			/	/	x	/	x	x	x	/	/	/
Dumping	x	x		/	/	/	x	x	x	x	x			/	/	x	/	x	x	x	/	/	/
Subsurface Drains & Ditches	x	x		/	x	x	x	x	/	x	x			/		x		x	/	x	/	/	/
Liners	x	x		x		x	x	x	x	x	x	/		/	x			x	x	x	/	/	/
Surface Water Technologies	/	x	x		x	x	x	x	x	x	x		x	/	/	/	/	/	/	/	/	/	/

Source: Arthur D. Little, Inc., 1982.

Grout curtains are installed principally to seal voids in porous or fractured rock in situations where other groundwater controls are impractical. Solutions or water-solid suspensions are injected under pressure into the ground, filling voids and reducing groundwater flow. Soil and geologic conditions determine the type of grout applied: cement, bentonite, and chemicals are common types; grouts specific to soil and other local conditions are epoxy resins, silicone rubbers, lime, fly ash and bituminous compounds. A grout curtain designed to eliminate groundwater flow is installed by first placing two or three rows of pipes in a grid pattern (as shown in Figure 96. Grout is then injected through the pipes at successive depths to fill pore spaces in the surrounding areas.

Sheet piling cutoff walls are constructed by driving web sections of steel sheet piling permanently into the ground. Each sheet pile is interlocking at its end by either a socket or a bowl and ball end. Sheet piles vary in length and shape, as shown in Figure 97. Sections are assembled before they are driven into the ground. Initially, they are not watertight due to rough fitting of the interlocking edges; however, in predominantly fine to medium grained soils, the joint connections soon fill with soil particles to reduce groundwater flow.

(b) Engineering Considerations

Slurry Walls

The most important engineering factors which influence the effectiveness of slurry walls are the characteristics of the slurry and the characteristics of the backfill (for SB walls). Viscosity is the most important property of the slurry. A viscosity of 40 seconds Marsh (i.e., 40 seconds for a volume of slurry to pass through a standard Marsh Funnel) is recommended for trench stability and proper filter cake formation (D'Appolonia, 1980). In addition, unit weight of the slurry is important. For SB slurry, a unit weight of 240 Kg/m^3 (15 lb/ft^3) is recommended to allow proper displacement by the backfill. For CE slurry, a unit weight of approximately 1920 kg/m^3 (120 lb/ft^3) is recommended (Sommerer and Kitchens, 1980). Slurry should be designed according to in situ soil and groundwater characteristics. Varying slurry additives are available to counteract adverse in situ conditions (e.g., to increase viscosity).

Permeability is the most important backfill characteristic. For SB walls, a minimum bentonite content of 1 percent, with at least 20 percent fines content, is recommended to give minimum permeability. In addition, using plastic fines, as opposed to nonplastic or low plasticity fines, can decrease permeability an additional two orders of magnitude. With plastic fines, permeabilities as low as 10^{-8} cm/sec are possible (D'Appolonia, 1980). As with slurry materials, compatibility of backfill materials with contaminated groundwater should be tested. Adjusting fines content or using already contaminated soils may help the wall resist attack of contaminated groundwater. The effect of various pollutants on SB backfill is shown in Table 36.

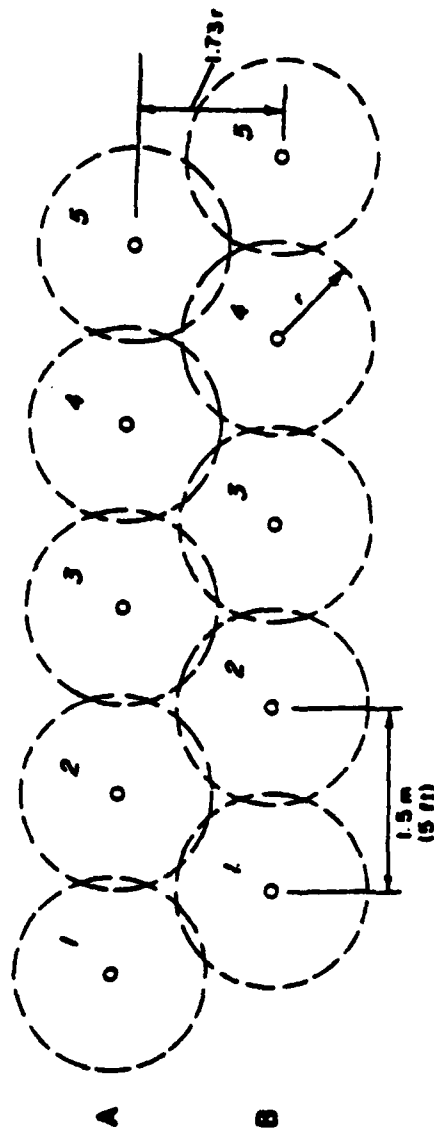


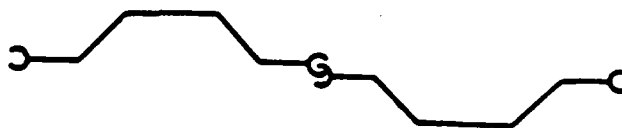
Figure 96. Typical Two-Row Grid Pattern for Grout Curtain

Source: EPA, 1982b.

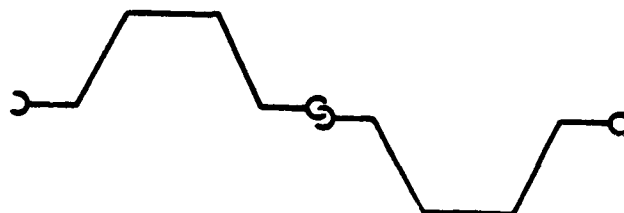
Straight Web Type



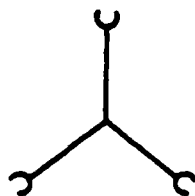
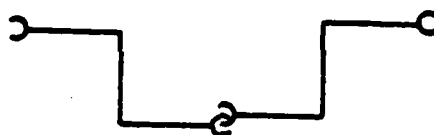
Arch Web Type



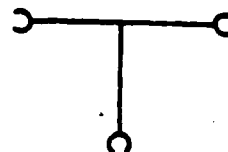
Deep Arch Web Type



Z-Type



Y-Fitting



T-Fitting

Figure 97. Steel Piling Shapes and Interlocks

Source: EPA, 1982 b.

TABLE 36. PERMEABILITY INCREASE DUE TO LEACHING WITH VARIOUS POLLUTANTS

Pollutant (1)	Filter Cake (2)	SB Backfill (silty or clayey) sand) 30% to 40% Fines (3)
CA++ or Mg++ at 1,000 ppm	N	N
CA++ or Mg++ at 10,000 ppm	M	M
NH ₄ NO ₃ at 10,000 ppm	M	M
HCL (1%)	N	N
H ₂ SO ₄ (1%)	M	N
HCL (5%)	M/H ^a	M/H ^a
NaOH (1%)	M	M
CaOH (1%)	M	M
NaOH (5%)	M	M/H ^a
Sea water	N/M	N/M
Brine (SG = 1.2)	M	M
Acid mine drainage (FeSO ₄ ; pH ~ 3)	N	N
Lignin (in CA++ solution)	N	N
Alcohol	H (failure)	M/H

^aSignificant dissolution likely.

Note: N = no significant effect, permeability increase by about a factor of 2 or less at steady state; M = moderate effect, permeability increase by factor of 2 to 5 at steady state; H = permeability increase by factor of 5 to 10.

Source: D'Appolonia, 1980

Grout Curtains

The effectiveness of a grout curtain and selection of grout materials depends primarily on soil permeability and grain size, chemical characteristics of the soil and groundwater, and grout strength requirements. Soils are considered unsuitable for grouting if more than 20 percent of the soil passes through a #200 sieve (Sommerer and Kitchens, 1980). Important properties of available grout materials are given in Table 37. Grout curtains are useful only under certain site specific conditions. In addition, they tend to be more expensive than slurry walls, and it is difficult to verify whether a contiguous impermeable curtain has actually been formed.

Sheet Piles

Steel sheet piles are typically useful to depths up to 15 meters in soils which are loosely packed and consist of primarily sand and gravel. Piling lifetime depends on groundwater characteristics. The pH of the groundwater is of particular concern. For steel pilings, pH of 5.8 to 7.8 is best, allowing a lifetime of up to 40 years, while a pH as low as 2.3 can reduce effective lifetime to 7 years or less (USEPA, 1982a).

(c) Groundwater Pumping

Description

Groundwater pumping utilizes one or more pumps to draw groundwater to the surface through a series of wells, forming a cone of depression in the groundwater table. Shallow well points or deep well systems may be used, dependent on the depth of the aquifer. Well point systems are used in shallow, unconfined aquifers. They consist of a series of riser pipes connected to a common header pipe and a centrifugal pump. A typical well point dewatering system is shown in Figure 98. Deep well systems can be used in confined or unconfined aquifers up to depths of several hundred meters.

Groundwater pumping can be used to lower the water table, contain a plume, or remove contaminated groundwater. It is often used in conjunction with other groundwater controls, such as impermeable barriers, for more effective groundwater control.

Engineering Considerations

The effect of a well or well system on a water table can be very difficult to predict. The following general equations can be used for estimating drawdown (s) under certain conditions (Freeze and Cherry, 1979).

TABLE 37. GROUT PROPERTIES

GROUT MATERIAL	CATALYST MATERIAL	UNCONFINED COMPRESSIVE STRENGTH (PSI) OF SETTING SOIL	VISCOSITY (CENTIPOISE)	SETTING TIME MINUTES	TOXICANT*	POLLUTANT**
SILICATE BASE						
LOW CONCENTRATION	BICARBONATE	10-50	1.5	0.1 - 300	NO	NO
LOW CONCENTRATION	HALLIBURTON CO. MATERIAL	10-50	1.5	5 - 300	NO	NO
LOW TO HIGH CONCENTRATION	SITOC - DIAMOND SHIMMOCK CHEMICAL CO.	10-500	4-40	5 - 300	NO	NO
LOW TO HIGH CONCENTRATION	CHLORIDE - JOOSTEN PROCESS	10-1000	30-50	0	NO	NO
LOW TO HIGH CONCENTRATION	ETHYL ACETATE SOLENTANONE & HALLIBURTON	10-500	4-40	5 - 300	NO	NO
LOW TO HIGH CONCENTRATION	AMONE-PROBIL 600	-	-	-	-	-
LOW TO HIGH CONCENTRATION	GELOC-3 H. BAKER CO.	10-500	4-25	2 - 200	NO	NO
LOW TO HIGH CONCENTRATION	GELOC - 3A	10-250	4-25	0.5 - 120	NO	NO
LIGNIN BASE						
BLACK-ALL	HALLIBURTON CO. MATERIAL	5-80	8-15	3 - 90	YES	YES
TEN	CEMENTATION CO. MATERIAL	50-500	2-4	5 - 120	YES	YES
TERRA-FIRM	INTRUSION CO. MATERIAL	10-50	2-5	10 - 300	YES	YES
LIGNOSOL	LIGNOSOL CO. MATERIAL	10-50	50	10 - 1000	YES	YES
FORMALDEHYDE BASE						
UREA-FORMALDEHYDE	HALLIBURTON CO. MATERIAL	OVER 1000	10	4 - 60	YES	YES
UREA-FORMALDEHYDE	AMERICAN CYANAMID CO. MATERIAL	OVER 500	13	1 - 60	YES	YES
RESORCINOL FORMAL-DEHYDE	CEMENTATION CO. MATERIAL	OVER 500	3.5	—	YES	YES
TANNIN - PARA-FORMALDEHYDE	BORDEN COMPANY HQ-3					
GEOSOL HQ-4 & HQ-5	BORDEN COMPANY MATERIAL					
UNSATURATED FATTY ACID BASE						
POLYTHIXON FPD	CEMENTATION CO. MATERIAL	OVER 500	10 - 80	25 - 360	NO	NO

* - A material which must be handled using safety precautions and/or protective clothing.
 ** - Pollutant to fresh water supplies contacted.

Source: Halliburton Services, 1976.

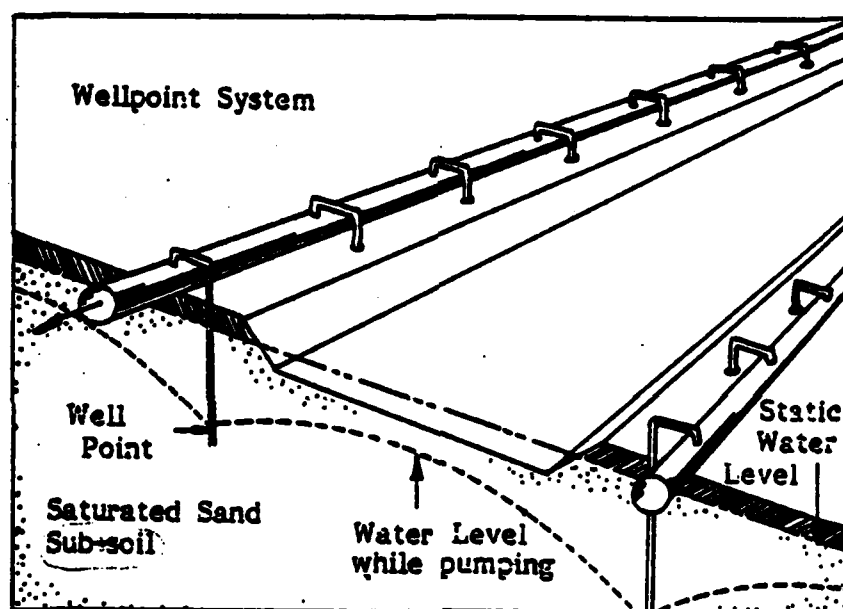


Figure 98. Well Point Dewatering System

Source: Sommerer and Kitchens, 1980

- In a confined, isotropic aquifer:

$$s = \frac{Q_w}{4 \pi T} W(u) \quad (20)$$

- In an unconfined aquifer at early time ($t < \text{a few minutes}$):

$$s = \frac{Q_w}{4 \pi T} W(u_A, n) \quad (21)$$

- In an unconfined aquifer at later time ($t > \text{a few minutes}$):

$$s = \frac{Q_w}{4 \pi T} W(u_B, n) \quad (22)$$

where:

$$u = u_A = \frac{r^2 S}{4 T t}$$

$$u_B = \frac{r^2 y}{4 T t}$$

$$r = \frac{r}{b^2} \quad \text{in an anisotropic aquifer}$$

$$n = \frac{r^2 k_1}{b^2 k_2} \quad \text{in an isotropic aquifer}$$

and:

- Q_w = pumping rate of the well
- T = transmissivity of the aquifer
- $W(u)$ = well function for confined aquifers
- $W(u_A, n)$ = type A well function
- $W(u_B, n)$ = type B well function
- r = radial distance from the well where drawdown is measured
- t = time from initial pumping at which drawdown is measured
- S = storativity of the aquifer
- y = specific yield of the aquifer
- b = depth of the aquifer before pumping
- k_1 = vertical hydraulic conductivity
- k_2 = horizontal hydraulic conductivity

Values for $W(u)$, $W(u_A, n)$ and $W(u_B, n)$ can be found in standard hydrology texts or engineering manuals. For $\mu < .01$, $W(u)$ can be approximated as:

$$W(u) = \ln \frac{2.246 T t}{r^2 S} \quad (23)$$

The previous equations are based on the following assumptions:

- the aquifer is homogeneous
- the aquifer is not leaky
- the well penetrates and is screened over the entire depth of the aquifer
- pumping rate is uniform over time
- only one aquifer is affected by the well
- there are no barriers or rivers within the radius of influence of the well
- flow to the well remains saturated for confined aquifers

If any of these assumptions is not valid for a particular well system, the simple drawdown equations are not valid. A hydrologist should be consulted to determine drawdown on a site-specific basis.

For a multiple well system, total drawdown at a given place and time is simply the added drawdown of each individual well such that (Freeze and Cherry, 1979):

$$S_{\text{total}} = \sum_{i=1}^n S_{\text{well}(i)} \quad (24)$$

Well point systems are practical at depths up to 10 meters, and most effective at 4.5 meters. Spacing is typically 1 to 2 meters and well points should be close enough together to maintain sufficient drawdown between the wells. Spacing and effectiveness will depend on site specific conditions (Sommerer and Kitchens, 1980).

Deep wells must be of sufficient diameter (at least 10 cm) to house a submersible pump and handle expected flow (Sommerer and Kitchens, 1980). Construction of deep wells is similar to the construction of monitoring wells, which is discussed in detail in Section IV.

(d) Leachate Collection

Description

Leachate collection technologies include:

- subsurface drains;
- drainage ditches;
- liners; and
- wells

Subsurface drains are constructed by placing tile or perforated pipe in a trench, surrounding it with gravel envelope, and backfilling with topsoil or clay. They have been used extensively to dewater construction sites. At remedial action sites, subsurface drains can be installed to collect leachate, as well as lower the water table for site dewatering. They have been used at Love Canal and other major remedial action sites for leachate collection.

Drainage ditches are open trenches designed to collect surface water runoff, collect flow from subsurface drains, or intercept lateral seepage of water or leachate through the site. They are considered preferable to subsurface drains when the slope of the flow is steep. Drainage ditches are generally simple to construct, but may require extensive maintenance to maintain operating efficiency (USEPA, 1982b).

Liners, although mentioned in the National Contingency Plan as a leachate control technique, are not generally applicable to remedial action sites. Liners are useful at newly constructed disposal facilities to protect groundwater from leachate migration. Construction of liners at existing, unlined sites, however, is extremely difficult. Bottom sealing techniques, such as pressure-injection grouting, are practical over a very limited range of hydrogeologic conditions and are generally undemonstrated as a remedial action technique. In addition, costs for bottom sealing are expected to be extremely high, and no method is currently available to determine whether the seal is complete (USEPA 1982b). In view of this, liners will not be further considered as a numerical action technique.

(e) Engineering Considerations

Subsurface Drains

Drain pipe material should be compatible with groundwater and leachate characteristics. In general, fired clay is more suitable for corrosive or high strength chemical wastes than plastic or metal pipe. In addition, an envelope of permeable material (typically gravel) should surround the drain pipe. Recommended minimum thickness of the drain envelope is 8 to 10 centimeters (3 to 4 inches). A typical envelope thickness is 14 centimeters (6 inches) and can be much larger. For example, at Love Canal the gravel envelope was about 66 centimeters thick (26 inches). The envelope of permeable material may be wrapped with a fabric to prevent clogging with soil (USEPA 1982b).

Drain depth is determined based on site specific conditions. In general, the deeper the drain, the wider the spacing that is possible (and, therefore, the fewer drains that are required). However, the cost of deeper drains with larger design flow should be compared with shallower drains with smaller design flow to determine the optimal number and depth of drains.

The distance between adjacent drains is primarily a function of drain depth, design flow (hydraulic capacity) of the drain, and soil

permeability. The equation normally used to determine drain spacing is (Linsley and Frazini, 1979):

$$L = \frac{4k (b^2 - a^2)}{Q} \quad (25)$$

where (see Figure 99):

- L = distance between adjacent drains (m)
- k = soil permeability (m/sec)
- Q = design flow per meter of drain (m³/sec/m of drain)
- a = height of drain above impermeable barrier (m)
- b = maximum height of water table above impermeable barrier (m)

This equation assumes steady state, one-dimensional flow through homogeneous soil. If these assumptions are not valid, spacing may be determined experimentally based on soil properties. Determining spacing based on two- or three-dimensional flow becomes a differential boundary value problem based on Laplace's equation. This can be solved using computer generated or published solutions (USEPA 1982b).

Design flow per meter of drain can be determined by performing a water balance to estimate the amount of water a drain will need to be able to transport. Manning's formula can then be used to determine pipe size.

Inflow to a pipe can also be roughly estimated as (Frogge and Sanders, 1977):

$$Q = \frac{DA (k)}{10} \quad (26)$$

where:

- Q = inflow to pipe (m³/sec)
- DA = area drained by pipe (m²)
- k = soil permeability (m/sec)

This should be used as a rule of thumb only.

Draining Ditches

Water level and flow velocity in drainage ditches depend on site specific characteristics and the function of the ditch. Factors which determine flow velocity include soil type, channel shape, grade and roughness, and sediment loading. The size of the ditch required can be determined using a water balance and Manning's formula. Ditch side slopes depend on soil stability and hazard of scour. Stabilization of side slopes by compaction, vegetation, or fabric liner may be necessary. Trapezoidal and parabolic cross-sections are generally considered most

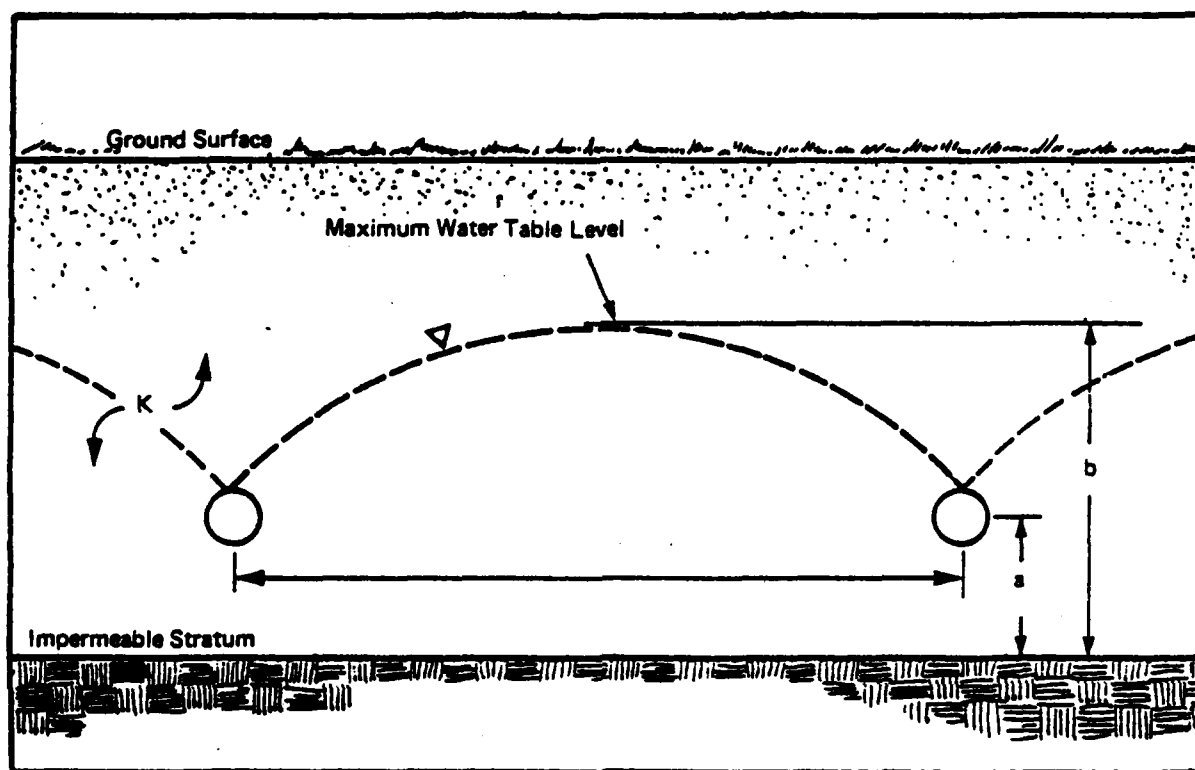


Figure 99. Spacing Equation Diagram

Source: Frogge and Sanders, 1977

stable. Maintenance of vegetation, side slopes, and depth (removal of obstruction or sediments) may be required (USEPA 1982a; USEPA 1982b).

(f) Removal

Description

Removal of the source of contamination may involve excavation of loose, drummed or tanked waste and contaminated soil, pumping of impounded liquids, and similar measures. Removal may be appropriate when the source is small, such as a leaky 500-gallon underground storage tank, when containment or treatment measures are not appropriate or cost effective in comparison, or when the hazards of not removing the source are acute.

Excavation of waste is the major removal technology. Although excavation at construction sites is a well-demonstrated technology, the application to hazardous waste sites presents some unique problems. The load-bearing capacity and fill density, which may be affected by the buried waste, should be considered before deciding to operate heavy equipment at the site. Landfilled drums must be handled with caution. If drums are punctured or already leaking, additional soil at the site can be contaminated. Sparks created by drum contact with grappling hooks can ignite flammable waste. Typically, drums are moved to a staging area for transfer, if necessary, to a secure drum or a tank truck.

Removal operations at a site may be hazardous and special precautions should be taken. Operators of equipment may be exposed to hazardous vapors and to direct contact with liquids, solids, and contaminated surfaces. Protective clothing, including respirators, may be required in some cases. Equipment may become contaminated and require decontamination before it can be taken offsite and used somewhere else.

Surface impoundment sludge bottoms and contaminated soils can be removed by dredging techniques such as centrifugal pumping and hydraulic pipeline dredges. Both methods are readily available and comparable in cost. The waste can be pumped directly to tank trucks as a low solid content sludge (less than 20 percent solids). If transport distances to a dewatering facility are large, it may be cost effective to dewater on site. Impoundments can be drained prior to sludge removal by pumping the liquid phase to a tank or other receptor. The uncovered sludge could present an odor problem. Dried sludges can be removed with the backhoe or dragline equipment discussed previously.

Engineering Considerations

Excavation of landfilled waste typically employs backhoes or dragline crane units. Backhoes are effective for removing compacted or loosely packed materials up to a depth of 21 meters. They offer accurate bucket placement and can be equipped for drum removal.

Dragline units are effective for the removal of unconsolidated materials to a depth of 18 meters. Optimal digging depth for both is considered to be 4.5 meters.

Removal of drummed or containerized waste poses special problems. Several approaches are available. Drums in good condition can simply be loaded on a truck and transported to an off site treatment, storage, or disposal (TSD) facility. The contents of corroded drums can be transferred to secure drums for offsite disposal and the former drums compacted for offsite disposal. A third alternative is to blend the contents of drummed waste in holding tanks and subsequently pump the blended materials into a tank truck for removal. Blending operations must be carefully monitored; extensive preblending and sampling of drums is necessary to screen for incompatible wastes.

(g) Surface Water Control

Many technologies are available to control surface water flow at a site. These include:

- dikes;
- terraces;
- channels;
- chutes and downpipes;
- grading;
- surface seals; and
- vegetation

These technologies perform five basic functions, which are summarized in Table 38. Management of surface water is important since the entire water balance can affect groundwater contamination problems. Remedial actions for groundwater contamination, therefore, may require one or more of these technologies to minimize the production of leachate and prevent off site contamination. Each of these technologies is described briefly below.

Dikes

Dikes are compacted earthen ridges designed to divert or retain surface water flow. They can be used to control floodwater or to control runoff. Design of flood control dikes (or levees) depends on the amount of flood protection required based on expected height of water and failure hazard. Runoff control dikes can be used either to intercept flow (with a 0-percent grade) or, with a positive grade, to divert flow to stabilized outlets. Dike height, spacing, and construction are the primary design parameters.

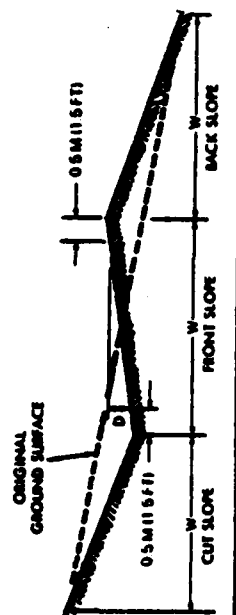
Terraces

Terraces are embankments or combinations of embankments and channels constructed across a slope. As shown in Figure 100, a variety of terrace cross-sections are possible depending on slope and site

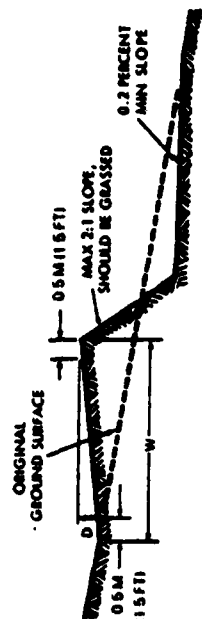
TABLE 38. SURFACE WATER TECHNOLOGIES

Technology	Primary Function					Collect and Transfer Water	Discharge Water
	Minimize Runon	Minimize Infiltration	Reduce Erosion	Protection from Flooding			
Flood control dikes				X			
Runoff control dikes	X		X				
Terraces	X		X				
Channels			X		X		
Chutes			X		X		
Downpipes			X		X		
Grading	X		X				
Surface seals		X					
Vegetation	X	X	X				
Seepage basins							X
Seepage ditches							X

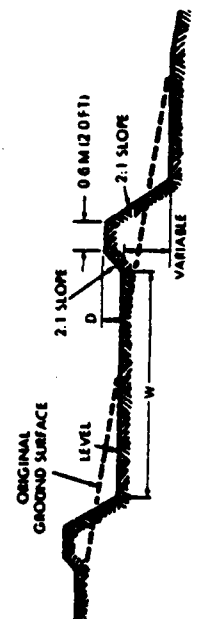
Source: Arthur D. Little, Inc., 1982.



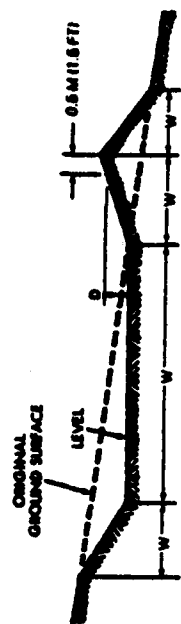
BROADBASE TERRACE CROSS SECTION



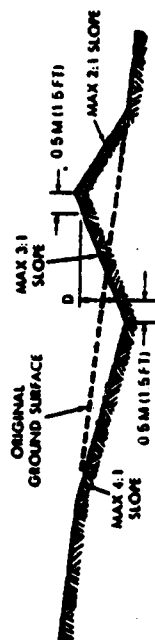
STEEP-BACKSLOPE TERRACE CROSS SECTION



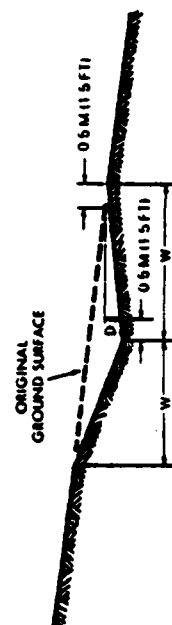
BENCH TERRACE CROSS SECTION



FLAT CHANNEL TERRACE OR ZINGG CONSERVATION BENCH TERRACE CROSS SECTION



NARROW-BASE TERRACE CROSS SECTION Slopes are the maximum allowable and should be grassed.



RIDGELESS CHANNEL TERRACE CROSS SECTION

Figure 100. Typical Terrace Cross-Sections

Source: ASAE, 1978,

specific requirements. Terraces can be used to intercept and divert surface flow away from a site and to control erosion by reducing slope length.

Channels

Channels are wide and shallow excavated ditches with trapezoidal, triangular, or parabolic cross sections. Diversion channels are used primarily to intercept runoff or reduce slope length. They may or may not be stabilized. Channels stabilized with vegetation or stone riprap (waterways) are used to collect and transfer diverted water off site or to on site storage or treatment.

Chutes and Downpipes

Chutes (or flumes) are open channels normally lined with bituminous concrete, portland cement, concrete, grouted riprap, or similar non-erodible material.

Downpipes (or downdrains) are drainage pipes constructed of rigid piping (such as corrugated metal) or flexible tubing of heavy duty fabric. They are installed with prefabricated entrance sections. Downpipes can also be open structures constructed by joining half sections of bituminous fiber or concrete pipe.

Chutes and downpipes are useful in transferring concentrated flows of surface runoff from one level of a site to a lower level without erosive damage. They generally extend downslope from earthen embankments and convey water to stabilized waterways or outlets located at the base of the slope. Downpipes are particularly useful in emergency situations since they can be quickly constructed during severe storms to handle excess flow when downslope waterways overflow and threaten the containment of hazardous waste (USEPA 1982b).

Grading

Grading is the general term for technologies used to modify the natural topography and runoff characteristics of a waste site. Grading primarily involves the use of heavy equipment (such as dozers, loaders, scrapers, and compacters) to spread and compact loose soil, roughen and loosen compacted soil, and modify the surface gradient. There are six basic grading techniques described in Table 39.

Grading has two primary applications:

- Slope Grade Construction: Excavation, spreading, compaction, and hauling are used to optimize the slope at a waste site such that surface runoff increases and infiltration and ponding decrease without significantly increasing erosion. This is of primary importance in the construction of surface seals and other waste covers.

- Preparation for Revegetation: Roughening techniques (scarification, tracking, and contour furrowing) are used to reduce runoff, thereby increasing infiltration, and make the soil receptive to seed or seedlings. This is an important aspect of offsite revegetation once an effective surface seal has been applied. These techniques can also be used offsite in conjunction with surface water diversion technologies to control runoff.

Surface Seals

Surface seals (caps or covers) are impermeable barriers placed over waste disposal sites to:

- reduce surface water infiltration
- reduce water erosion
- reduce wind erosion and fugitive dust emissions
- contain and control gases and odors
- provide a surface for vegetation and other postclosure uses

Various impermeable materials may be used, including soils and clays, admixtures (e.g., asphalt concrete, soil cement), and polymeric membranes (e.g., rubber and plastic linings).

Typical surface seals are composed of several layers, including:

- barrier layer to restrict the passage of water or gas. The barrier has low permeability and is usually composed of clayey soil or a synthetic membrane;
- buffer soil layer above and/or below the barrier layer to protect the barrier layer from cracking, drying, tearing, or from being punctured. It is usually a sandy soil;
- filter layer, made of intermediate grain sizes, to prevent fine particles of the barrier from penetrating and sifting through the coarser buffer layer;
- gas channeling layer of sand and gravel placed immediately above the waste to allow generated gases to escape or be collected. Pipe and trench vents can be used in conjunction with this layer for gas and odor control;
- top soil layer for growth of vegetation.

TABLE 39. GRADING TECHNIQUES

Technique	Description	Use	Equipment
Excavation	soil removal	slope grade construction	dozer, loader, scraper
Spreading	soil application smoothing	slope grade construction	dozer, loader, compactor,
Compaction	compacts soil increases density	slope grade construction	dozer, loader, compactor
Scarification	roughening technique loosens soil	preparation for revegetation increases infiltration	loader, tractor, harrow
Tracking	roughening technique grooves soil along contour	preparation for revegetation increases infiltration	cleated crawler tractor
Contour Furrowing	roughening technique creates small depressions in soil along contour	preparation for revegetation increases infiltration	dozer

Source: Arthur D. Little, Inc., 1982.

Vegetation

Vegetation can perform four basic functions:

- it can stabilize soil and earthen structures against wind and water erosion by intercepting rainfall, slowing runoff, and holding soil together with a tight root system;
- it can reduce the quantities of water available for runoff through interception, infiltration, uptake, and transpiration;
- it can treat contaminated soil and leachate through the uptake and removal of waste constituents, nutrients, and water from the soil;
- it can improve the aesthetic appearance of the site.

Plants used for revegetation include various types of grasses, legumes, shrubs, and trees. A revegetation program involves careful plant selection, land preparation (such as increasing soil depth, grading, fertilizing and tilling), seeding, and maintenance.

SECTION VII

INFORMATION SOURCES

The information which needs to be evaluated during analysis of a groundwater contamination problem includes a description of the physical framework through which water is moving, a description of the hydrologic system and documentation of present and past base operations, including construction details.

Data and interpretive reports regarding the physical framework and hydrologic system would generally be available from federal, state, or local governmental agencies that are responsible for natural resource or environmental studies. Information may also be available from engineering or consulting firms that may have performed local specialized studies. Site use and construction information should be available through the office of the Base Engineer.

1. GEOLOGIC FRAMEWORK AND HYDROLOGIC SYSTEM

Information regarding the geologic framework and hydrologic system is generally available from federal and state geologic or natural resource surveys. The type of information which can be obtained from each agency will range from fundamental data, such as well logs and water level measurements, to specialized technical reports. In some states, the local state agency will be the principal information source, and in other states, the federal agency will provide the most information. Tables 40 and 41 list the addresses of the state geologists and the district offices of the Water Resources Division of the U.S. Geological Survey. In addition to providing in-house data and reports regarding local hydrogeologic conditions, the U.S. Geological Survey district offices provide access to national water-related databases, such as NAWDEX and WATSTORE, as well as providing a convenient access to other geological survey reports and information.

NAWDEX (National Water Data Exchange) is a computerized data system that can identify sources of water data, locations of sites at which water data are being collected, and assist users of water data in locating and procuring data that meet their specific criteria and are in the geographic area of interest. WATSTORE (National Water Data Storage and Retrieval System) provides access to streamflow, water quality and groundwater data. Access to this data base can be made through computer facilities of the U.S. Geological Survey or by establishing a separate user account. U.S. Geological Survey Circular 777, entitled "Guide to Obtaining Information from the U.S. Geological Survey," provides more detailed instructions about obtaining information from the U.S. Geological Survey.

Local engineering and/or consulting firms may have performed specialized studies in the area of interest and may have geologic or hydrologic data available. The Base Engineer may have information

TABLE 40. ADDRESSES OF STATE GEOLOGISTS

(from the 1980 Directory of the Association of American State Geologists)

ALABAMA (205)349-2852

Thomas J. Joiner
Geol. Survey of Alabama
P. O. Drawer 0
University, AL 35486

ALASKA (907)279-1433

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Div. of Geology and
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Anchorage, AK 99501

ARIZONA (602)626-2733

Larry D. Fellows
Bureau of Geology and
Mineral Technology
Geol. Survey Branch
845 N. Park Avenue
Tucson, AZ 85719

ARKANSAS (501)371-1488

Norman F. Williams
Arkansas Geol. Commission
Vardelle Parham Geol. Center
3815 W. Roosevelt Road
Little Rock, AR 72204

CALIFORNIA (916)445-1923

F. Davis
Div. of Mines & Geology
Calif. Dept. of Conservation
1416 9th Street, Room 1341
Sacramento, CA 95814

COLORADO (303)839-2611

John W. Rold
Colorado Geological Survey
1313 Sherman St., Room 715
Denver, CO 80203

CONNECTICUT (203)566-3540

Hugo F. Thomas
Conn. Geol. & Natural
History Survey
State Office Bldg., Room 553
165 Capitol Avenue
Hartford, CT 06115

FLORIDA (904)488-4191

Charles W. Hendry, Jr.
Bureau of Geology
903 W. Tennessee St.
Tallahassee, FL 32304

GEORGIA (404)656-3214

William McLemore
Geol. and Water
Resources Division
Dept. of Natural Resources
19 Dr. Martin Luther King,
Jr. Drive, S.W.
Atlanta, GA 30334

HAWAII (808)548-7533

Robert T. Chuck
Div. of Water & Land Dev.
P. O. Box 373
Honolulu, HI 96809

IDAHO (208)885-6785

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and Geology
Moscow, ID 83843

ILLINOIS (217)333-5111

Jack A. Simon
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Survey
121 Natural Resources Bldg.
Urbana, IL 61801

INDIANA (812)337-2862

John B. Patton
Dept. of Natural Resources
Indiana Geological Survey
611 North Walnut Grove
Bloomington, IN 47401

IOWA (319)338-1173

Stanley C. Grant
Iowa Geological Survey
123 N. Capitol
Iowa City, IA 52242

KENTUCKY (606)622-3270

Donald C. Haney
Kentucky Geol. Survey
University of Kentucky
311 Breckinridge Hall
Lexington, KY 40506

LOUISIANA (504)342-6754

Charles G. Groat
Louisiana Geol. Survey
Box G, Univ. Station
Baton Rouge, LA 70893

MAINE (207)269-2801

Walter Anderson
Maine Geological Survey
State Off Bldg, Rm 211
Augusta, ME 04330

MARYLAND (301)235-0771

Kenneth N. Weaver
Maryland Geol. Survey
Merryman Hall
Johns Hopkins University
Baltimore, MD 21218

MASSACHUSETTS

Joseph A. Sinnott
Dept. of Environ.
Quality Engineering
Div of Waterways, Rm 532
100 Nashua Street
Boston, MA 02114

MICHIGAN (517)373-1256

Arthur E. Slaughter
Mich. Dept. of Nat. Res.
Geological Survey Div.
P. O. Box 30028
Lansing, MI 48909

MINNESOTA (612)373-3372

Matt Walton
Minnesota Geol. Survey
1633 Eustis Street
St. Paul, MN 55108

TABLE 40. (CONTINUED)

<u>DELAWARE</u> (302)738-2833 Robert R. Jordan Delaware Geological Survey University of Delaware Newark, DE 19711	<u>KANSAS</u> (913)864-3965 William W. Hambleton State Geol. Survey of Kansas Raymond C. Moore Hall 1930 Avenue A, Campus West Lawrence, KS 66044	<u>MISSISSIPPI</u> (601)354-6228 William H. Moore Miss. Geol., Econ., & Topo. Survey P. O. Box 4915 Jackson, MS 39216
<u>MISSOURI</u> (314)364-1752 Wallace B. Howe Div. of Geol. & Land Survey P. O. Box 250 Rolla, MO 65401	<u>NORTH DAKOTA</u> (701)777-2231 Lee C. Gerhard N. Dakota Geological Survey University Station Grand Forks, ND 58202	<u>TENNESSEE</u> (615)741-2726 Robert E. Hershey Dept. of Conservation Division of Geology G-5 State Office Bldg. Nashville, TN 37219
<u>MONTANA</u> (406)792-8321 Sid Groff Mont. Bureau of Mines & Geology Montana College of Mineral Science & Technology Butte, MT 59701	<u>OHIO</u> (614)466-5344 Horace R. Collins Ohio Div. of Geol. Survey Fountain Square, Bldg. B Columbus, OH 43224	<u>TEXAS</u> (512)471-1534 W. L. Fisher Bureau of Econ. Geology Univ. Station, Box X Austin, TX 78712
<u>NEBRASKA</u> (402)472-3471 Vincent H. Dreeszen Conservation & Survey Div. University of Nebraska Lincoln, NE 68508	<u>OKLAHOMA</u> (405)325-3031 Charles J. Mankin Oklahoma Geol. Survey 830 Van Vleet Oval, Rm 163 Norman, OK 73019	<u>UTAH</u> (801)581-6831 Donald T. McMillan Utah Geol. & Min. Survey 606 Black Hawk Way Salt Lake City, UT 84108
<u>NEVADA</u> (702)784-6691 John Schilling Nevada Bureau of Mines & Geology University of Nevada Reno, NV 89557	<u>OREGON</u> (503)229-5580 Donald A. Hull State Dept. of Geology & Mineral Industries 1069 State Office Bldg. 1400 S.W. Fifth Avenue Portland, OR 97201	<u>VERMONT</u> (802)828-3357 Charles A. Ratte Agency of Environmental Conservation 5 Court Street Montpelier, VT 05602
<u>NEW HAMPSHIRE</u> (603)862-1216 Glenn W. Stewart Office of State Geologist James Hall Univ. of New Hampshire Durham, NH 03824	<u>PENNSYLVANIA</u> (717)787-2169 Arthur A. Socolow Bureau of Topo. & Geol. Survey Dept. of Environ. Resources P. O. Box 2357 Harrisburg, PA 17120	<u>VIRGINIA</u> (804)293-5121 Robert C. Milici Virginia Div. of Univ. of Mineral Resources P. O. Box 3667 Charlottesville, VA 22903
<u>NEW JERSEY</u> (609)292-2576 Kemble Widmer New Jersey Bureau of Geol. & Topography P. O. Box 1390 Trenton, NJ 08625	<u>PUERTO RICO</u> Director Servicio Geologico de P.R. Dept. de Recursos Naturales Apartado 5887, Puerta de Tierra San Juan, PR 00906	<u>WASHINGTON</u> (206)753-6183 Vaughn E. Livingston, Jr. Dept of Natural Resources Geology & Earth Resources Division Olympia, WA 98504

TABLE 40. (CONCLUDED)

NEW MEXICO (505)835-5420

Frank E. Kottlowski
Mexico Bureau of Mines
& Mineral Resources
New Mexico Tech
Socorro, NM 87801

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State Education Bldg.
Albany, NY 12234

N. CAROLINA (919)733-3833

Stephen G. Conrad
N. Carolina Dept. of Nat.
Res. & Community Develop.
P. O. Box 27687
Raleigh, NC 27611

RHODE ISLAND

Robert L. McMaster
Assoc. State Geologist for
Marine Affairs
Grad. Schl. of Oceanography
Kingston, RI 02881

S. CAROLINA (803)758-6431

Norman K. Olson
S. Carolina Geol. Survey
State Development Board
Harbison Forest Road
Columbia, SC 29210

SOUTH DAKOTA (605)624-4471

Duncan J. McGregor
S.D. State Geol. Survey
Science Center
Univ. of South Dakota
Vermillion, SD 57069

W. VIRGINIA (304)292-6331

Robert B. Erwin
W. Va. Geol. & Econ. N.
P. O. Box 879
Morgantown, WV 26505

WISCONSIN (608)262-1705

Meredith E. Ostrom
Wisc. Geol. & Natural
History Survey
1815 University Ave.
Madison, WI 53706

WYOMING (307)742-2054

Daniel N. Miller, Jr.
Wyoming Geol. Survey
Box 3008, Univ. Station
Laramie, WY 82071

TABLE 41. ADDRESSES OF THE DISTRICT OFFICES OF THE U.S. GEOLOGICAL
SURVEY WATER RESOURCES DIVISION

University of Alabama
Oil & Gas Bldg. - Room 202
P. O. Box V
Tuscaloosa, ALABAMA 35486
(205) 752-8104

218 E. Street
Anchorage, ALASKA 99501
(907) 271-4138

Federal Building
301 W. Congress Street
Tucson, ARIZONA 85701
(501) 378-6391

855 Oak Grove Avenue
Menlo Park, CALIFORNIA 94025
(415) 323-8111

Building 53
Denver Federal Center
Lakewood, COLORADO 80223
(303) 234-5092

135 High Street - Room 235
Hartford, CONNECTICUT 06103
(203) 244-2528

Subdistrict - District Office/MD
Federal Building - Room 1201
Dover DELAWARE 19901
(302) 734-2506

325 John Knox Road - Suite F-240
Tallahassee, FLORIDA 32303
(904) 386-1118

Suite B
6481 Peach Tree, Indust. Blvd.
Doraville, GEORGIA 30360
(404) 221-4858

Field Headquarters
4398D Loke St., P. O. Box 1856
Lihue, Kauai, GUAM 96766

Subdistrict
U.S. Navy Public Works Center
FPO S.F. 96630 - P. O. Box 188
Agana, GUAM 96910

P. O. Box 50166
300 Ala Moana Blvd. - Room 6110
Honolulu, HAWAII 96850
546-8331

P. O. Box 2230
Idaho Falls, IDAHO 83401
(208) 526-2438

P. O. Box 1026
605 N. Nek Street
Champaign, ILLINOIS 61820
(217) 398-5353

1819 North Meridan Street
Indianapolis, INDIANA 46202
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Lawrence, KANSAS 66045
(913) 864-4321

Table 41. (CONTINUED)

Federal Building - Room 572
600 Federal Place
Louisville, KENTUCKY 40202
(502) 582-5241

6554 Florida Boulevard
Baton Rouge, LOUISIANA 70896
(504) 389-0281

District Office in Mass.
26 Ganneston Drive
Augusta, MAINE 04330
(207) 623-4797

208 Carroll Building
8600 Lasalle Road
Towson, MARYLAND (301) 828-1535

150 Causeway Street, Suite 1001
Boston, MASSACHUSETTS 02114
(617) 223-2822

6520 Mercantile Way - Suite 5
Lansing, MICHIGAN 48910
(517) 372-1910

702 Post Office Building
St. Paul, MINNESOTA 55101
(612) 725-7841

Federal Building, Suite 710
100 West Capitol Street
Jackson, MISSISSIPPI 39201
(601) 969-4600

Mail Stop 200
1400 Independence Road
Rolla, MISSOURI 65401
(314) 341-0824

Federal Building, Drawer 10076
Helena, MONTANA 59601
(406) 559-5263

Fed. Bldg/Courthouse - Rm 406
100 Centennial Mall North
Lincoln, NEBRASKA 68508
(402) 471-5082

Federal Building - Room 227
705 North Plaza Street
Carson City, NEVADA 89701
(702) 882-1388

Subdistrict - Dist. Off./Mass
Federal Building - 210
55 Pleasant Street
Concord, NEW HAMPSHIRE 03301

Federal Building - Room 436
402 E. State St. - P. O. Box 1238
Trenton, NEW JERSEY 08607
(609) 989-2162

Western Bank Building
505 Marquette, NW
Albuquerque, NEW MEXICO 87125

236 U.S. Post Office/Courthouse
P. O. Box 1350
Albany, NEW YORK 12201
(518) 472-3107

Century Station - Room 436
Post Office Building
P. O. Box 2857
Raleigh, NORTH CAROLINA 27602
(919) 755-4510

821 E. Interstate Avenue
Bismarck, NORTH DAKOTA 58501
(701) 255-4011

975 West Third Avenue
Columbus, OHIO 43212
(614) 469-5553

215 NW 3rd - Room 621
Oklahoma City, OKLAHOMA 73102
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(Mail) P. O. Box 3202
Ship-830 NE Holladay St., 97232
Portland, OREGON 97208
(503) 231-5242

Table 41. (CONCLUDED)

Federal Building - 4th Floor
P. O. Box 1107
Harrisburg, PENNSYLVANIA 17108
(717) 782-4514

Building 652, Ft. Buchanan
G.P.O. Box 4424
San Juan, PUERTO RICO 00936
(809) 783-4660

District Office in Mass.
Federal Bldg. & U.S. P. O.
Room 224
Providence, RHODE ISLAND 02903
(401) 528-4655

Strom Thurmond Federal Building
1835 Assembly Street - Suite 658
Columbia, SOUTH CAROLINA 29201
(803) 765-5966

Federal Building - Room 308
200 4th Street, S.W.
Huron, SOUTH DAKOTA 57350
(605) 352-8651

U.S. Courthouse
U.S. Federal Building-A-413
Nashville, TENNESSEE 37203
(615) 251-5424

Federal Building - 649
300 East 8th Street
Austin, TEXAS 78701
(512) 397-5766

Administration Building - 1016
1745 West 1700 South
Salt Lake, UTAH 84104
(801) 524-5663

District Office in Mass.
U.S. Post Office/Courthouse
Rooms 330B and 330C
Montpelier, VERMONT 05602
(802) 229-4500

200 West Grace Street - Room 304
Richmond, VIRGINIA 23220
(804) 771-2427

1201 Pacific Avenue - Suite 600
Tacoma, WASHINGTON 98402
(206) 593-6510

Federal Bldg./U.S. Courthouse
500 Quarrier St., East - Room 3017
Charlestown, WEST VIRGINIA 25301
(304) 343-6181

1815 University Building
Madison, WISCONSIN 53706
(608) 262-2488

P. O. Box 1125
J. C. O'Mahoney Federal Center
2120 Capitol Avenue - Room 5017
Cheyenne, WYOMING 82001
(307) 778-2220

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GROUNDWATER CONTAMINATION RESPONSE GUIDE VOLUME 2 DESK

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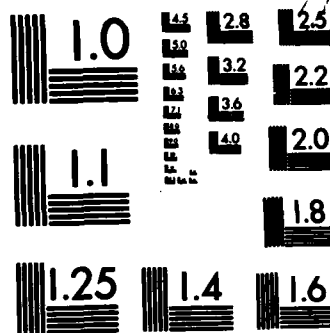
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

regarding any specialized engineering or consulting services that may have been performed on the base.

Soils information, including soil maps, types, physical characteristics, and depths is available from the Soil Conservation Service of the U.S. Department of Agriculture. Table 42 lists the addresses of various offices of the Soil Conservation Service.

2. SITE INFORMATION

Site information includes site construction information, as well as site use information. Construction information, such as the location of buried utilities, storage tanks, and pipelines should be available from the Base Engineer or local utility companies. This information is necessary to identify potential sources of contamination, to identify areas where drilling is precluded, and to identify those areas where construction activities may have altered the water-bearing characteristics of the natural geologic materials sufficiently to affect the groundwater flow direction.

Information regarding past operations on the base needs to be evaluated to identify possible past sources of contamination, such as abandoned landfills, evaporation pits, or storage areas. Comparison of current and older base engineering records and plans may be useful in interpreting changes in base operation. Aerial photographs taken at different times may also provide information regarding past changes in base operations, particularly with respect to changes in disposal operations. Aerial photographs and other remotely sensed imagery are generally available from the EROS Data Center and the National Cartographic Information Center. General assistance and identification of local sources of information can be obtained from:

National Cartographic Information Center (NCIC)

Headquarters

U.S. Geological Survey

507 National Center

(703) 860-6045

Room 1-C-107

12201 Sunrise Valley Drive

Reston, VA 22092

EROS Data Center

User Services Unit

(605) 594-6511

Sioux Falls, SD 57198

TABLE 42. ADDRESSES OF STATE OFFICES OF THE SOIL
CONSERVATION SERVICE

ALABAMA, Auburn 36830
Wright Building
138 South Gay Street
P. O. Box 311
(205) 821-8070

ALASKA, Anchorage 99504
Suite 129, Professional Bldg.
2221 E. Northern Lights Blvd.
(907) 276-4246

ARIZONA, Phoenix 85025
230 N. 1st Avenue
3008 Federal Building
(602) 261-6711

ARKANSAS, Little Rock 72203
Federal Building, Room 5029
700 West Capitol Street
P. O. Box 2323
(501) 378-5445

CALIFORNIA, Davis 95616
2828 Chiles Road
(916) 758-2200, ext. 210

COLORADO, Denver 80217
2490 W. 26th Avenue
P. O. Box 17107
(303) 837-4275

CONNECTICUT, Storrs 06268
Mansfield Professional Park
Route 44A
(203) 429-9361/9362

DELAWARE, Dover 19901
Treadway Towers, Suite 2-4
9 East Loockerman Street
(302) 678-0750

FLORIDA, Gainesville 32602
Federal Building
P. O. Box 1208
(904) 377-8732

GEORGIA, Athens 30603
Federal Building
355 E. Hancock Avenue
P. O. Box 832
(404) 546-2274

HAWAII, Honolulu 96850
300 Ala Moana Blvd.
Room 4316
P. O. Box 5004
(808) 546-3165

IDAHO, Boise 83702
304 North 8th Street, Rm 345
(208) 384-1601, ext. 1601

ILLINOIS, Champaign 61820
Federal Building
200 W. Church Street
P. O. Box 678
(217) 356-3785

INDIANA, Indianapolis 46224
Atkinson Square W. Suite 2200
5610 Crawfordsville Road
(317) 269-3785

IOWA, Des Moines 50309
693 Federal Building
210 Walnut Street
(515) 862-4260

KANSAS, Salina 67401
760 South Broadway
P. O. Box 600
(913) 825-9535

KENTUCKY, Lexington 40504
333 Waller Avenue
(606) 233-2749, ext. 2749

LOUISIANA, Alexandria 71301
3737 Government Street
P. O. Box 1630
(318) 448-3421

MAINE, Orono 04473
USDA Building
University of Maine
(207) 866-2132/2133

MARYLAND, College Park 20740
Room 522, Hartwick Building
4321 Hartwick Road
(301) 344-4180

Table 42. (CONTINUED)

MASSACHUSETTS, Amherst 01002
29 Cottage Street
(413) 549-0650

MICHIGAN, East Lansing 48823
1405 South Harrison Road
Room 101
(517) 372-1910, ext. 242

MINNESOTA, St. Paul 55101
200 Federal Bldg. & U.S. Courthouse
316 North Robert Street
(612) 725-7675

MISSISSIPPI, Jackson 39205
Milner Building, Room 590
210 South Lamar Street
P. O. Box 610
(601) 969-4330

MISSOURI, Columbia 65201
555 Vandiver Drive
(314) 442-2271, ext. 3155

MONTANA, Bozeman 59715
Federal Building
P. O. Box 970
(406) 587-5271, ext. 4322

NEBRASKA, Lincoln 68508
Federal Building
U.S. Courthouse, Room 345
(402) 471-5301

NEVADA, Reno 89505
U.S. Post Office Bldg., Room 308
P. O. Box 4850
(702) 784-5304

NEW HAMPSHIRE, Durham 03824
Federal Building
(603) 868-7581

NEW JERSEY, Somerset 08873
1370 Hamilton Street
P. O. Box 219
(201) 246-1205, ext. 20

NEW MEXICO, Albuquerque 87103
517 Gold Avenue, SW
P. O. Box 2007
(505) 766-2173

NEW YORK, Syracuse 13260
U.S. Courthouse & Federal Bldg.
100 S. Clinton Street, Room 771
(315) 423-5493

NORTH CAROLINA, Raleigh 27611
310 New Bern Avenue, Federal Bldg.
Room 544, P. O. Box 27307
(919) 755-4165

NORTH DAKOTA, Bismarck 58501
Federal Bldg. - Rosser Ave & 3rd St
P. O. Box 1458
(701) 255-4011, ext. 421

OHIO, Columbus 43215
200 No. High Street, Room 522
(614) 469-6785

OKLAHOMA, Stillwater 74074
Agriculture Building
Farm Road & Brumley Street
(405) 624-4360

OREGON, Portland 97209
Federal Office Building
1220 SW 3rd Avenue
(503) 221-2751

PENNSYLVANIA, Harrisburg 17108
Federal Bldg. & Courthouse
Box 985, Federal Square Station
(717) 782-4403

PUERTO RICO, Hato Rey 00918
Federal Office Bldg., Room 633
Mail: GPO Box 4868
Puerto Rico, San Juan 00936
(809) 753-4206

RHODE ISLAND, West Warwick 02893
46 Quaker Lane
(401) 828-1300

TABLE 42. (CONCLUDED)

SOUTH CAROLINA, Columbia 29210
240 Stoneridge Drive
(803) 765-5681

SOUTH DAKOTA, Huron 57350
Federal Bldg., 200 4th St., SW
P. O. Box 1357
(605) 352-8651

TENNESSEE, Nashville 37203
675 U.S. Courthouse
(615) 749-5471

TEXAS, Temple 76501
W. R. Poage Federal Building
101 S. Main Street, P. O. Box 648
(817) 773-1711, ext. 331

UTAH, Salt Lake City 84138
4012 Federal Bldg - 125 S. State S
(801) 524-5051

VERMONT, Burlington 05401
1 Burlington Square, Suite 205
(802) 862-6501, ext. 6261

VIRGINIA, Richmond 23240
Federal Bldg., Room 9201
400 N. 8th Street - P. O. Box 10026
(804) 782-2457

WASHINGTON, Spokane 99201
360 U.S. Courthouse
W. 920 Riverside Avenue
(509) 456-3711

WEST VIRGINIA, Morgantown 26505
75 High Street, P. O. Box 865
(304) 599-7151

WISCONSIN, Madison 53711
4601 Hammersley Road
(608) 252-5351

WYOMING, Casper 82601
Federal Office Bldg., P.O. Box 2440
(307) 265-5550, ext. 3217

TECHNICAL SERVICE CENTERS

MIDWEST

NEBRASKA, Lincoln 68508
Federal Bldg.-U.S. Courthouse, Rm 393
Phone: 541-5346 (FTS)
402-471-5361 (CML)

WEST

OREGON, Portland 97209
511 N.W. Broadway
Phone: 423-2824 (FTS)
503-221-2824 (CML)

NORTHWEST

PENNSYLVANIA, Broomall 19008
1974 Sproul Road
Phone: 596-5783 (FTS)
215-596-5710 (CML)

SOUTH

TEXAS, Ft. Worth 76115
Ft. Worth Federal Center
P. O. Box 6567
Phone: 817-334-5456 (FTS & CML)

CARTOGRAPHIC UNITS

(Not located at TSC)

MARYLAND, Lanham 20782
10,000 Aerospace Road
Phone: 301-436-8756 (FTS & CML)

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<u>No.</u>	<u>Title</u>	<u>Report No.</u>	<u>Date</u>
1.	Evaluating Cover Systems for Solid and Hazardous Waste	SW-867	1980
2.	Hydrologic Simulation on Solid Waste Disposal Sites	SW-868	1980
3.	Landfill and Surface Impoundment Performance Evaluation	SW-869	1980
4.	Lining of Waste Impoundment and Disposal Facilities	SW-870	1980
5.	Management of Hazardous Waste Leachate	SW-871	1981
6.	Guide to the Disposal of Chemically Stabilized and Solidified Wastes	SW-872	1981
7.	Closure of Hazardous Waste Surface Impoundment	SW-873	1981
8.	Design and Management of Hazardous Waste Land Treatment Facilities	SW-874	1981
9.	Soil Properties, Classification and Hydraulic Conductivity Testing	SW-875	1981
10.	Solid Waste Leaching Procedures Manual	Draft	1981
11.	Landfill Closure Manual	Draft	1981

**U.S. Environmental Protection Agency Oil and Hazardous Materials Spills
Branch, Hazardous Spills Reports:**

OHMSB Code	Date	Title	EPA Report Number NTIS Number
HR-1	Nov. '70	Control of Spillage of Hazardous Polluting Substances	EPA - 15090 F OZ 10/70 NTIS - PB-197 596/OBA PC A18/MF A01
HR-2	Aug. '72	Rapid Detection System for Organophosphates and Carbamate Insecticides in Water	EPA - R2-72-010 NTIS - PB-214 764/3BA PC A04/MF A01
HR-3	Mar. '73	Control of Hazardous Chemical Spills by Physical Barriers	EPA - R2-73-185 NTIS - PB-221 493/OBA PC A05/MF A01
HR-4	May '73	Feasibility of Plastic Foam Plugs for Sealing Leaking Chemical Containers	EPA - R2-73-251 NTIS - PB-222 627/2BA PC GPO/MF A01
HR-5	Sep. '73	Treatment of Hazardous Materials Spills with Floating Mass Transfer Media	EPA - 670/2-73-078 NTIS - PB-228 050/AS PC GPO/MF A01
HR-6	Dec. '74	Evaluation of MTF for Testing Hazardous Material Spill Control Equipment	EPA - 670/2-74-073 NTIS - PB-240 762/5BA PC A14/MF A01
HR-7	Apr. '75	Feasibility of 5 gpm Dynactor/Magnetic Separator System to Treat Spilled Hazardous Materials	EPA - 670/2-75-004 NTIS - PB-241 080/1BA PC A03/MF A01
HR-8	Jun. '75	Methods to Treat, Control and Monitor Spilled Hazardous Materials	EPA - 670/2-75-042 NTIS - PB-243 386/OBA PC A07/MF A01

HR-9	Jun. '75	Guidelines for the Disposal of Small Quantities of Unused Pesticides	EPA - 670/2-75-057 NTIS - PB-244 557/5BA PC A15/MF A01
HR-10	Jul. '76	Development of a Mobile Treatment System for Handling Spilled Hazardous Materials	EPA - 600/2-76-109 NTIS - PB-256 707/1BA PC A05/MF A01
HR-11	Sep. '76	Removal and Separation of Spilled Hazardous Materials from Impoundment Bottoms	EPA - 600/2-76-245 NTIS - PB-266 140/3BE PC A05/MF A01
HR-12	Dec. '76	Prototype System for Plugging Leaks in Ruptured Containers	EPA - 600/2-76-300 NTIS - PB-267 245/9BE PC A06/MF A01
HR-13	Aug. '77	Emergency Collection System for Spilled Hazardous Materials	EPA - 600/2-77-162 NTIS - PB-272 790/7BE PC A05/MF A01
HR-14	Aug. '77	Heavy Metal Pollution from Spillage at Ore Smelters and Mills	EPA - 600/2-77-171 NTIS - PB-272 639/6BE PC A06/MF A01
HR-15	Aug. '77	Multipurpose Gelling Agent and its Application to Spilled Hazardous Materials	EPA - 600/2-77-151 NTIS - PB-272 763/4BE PC A04/MF A01
HR-16	Oct. '77	In Situ Treatment of Hazardous Material Spills in Flowing Streams	EPA - 600/2-77-164 NTIS - PB-274 455/5 BE PC A04/MF A01
HR-17	Nov. '77	Evaluation of "CAN-1", a Warning Device for Organophosphate Hazardous Material Spills	EPA - 600/2-77-219 NTIS - PB-276 647/5 BE PC A04/MF A01
HR-18	Nov. '77	Performance Testing of Spill Control Devices on Floatable Hazardous Materials	EPA - 600/2-77-222 NTIS - PB-276 581/6BE PC A08/MF A01

HR-19	Nov. '77	Manual for the Control of Hazardous Materials Spills: Vol. I Spill Assessment and Water Treatment Techniques	EPA - 600/2-77-227 NTIS - 276 734/1BE PC A21/MF A01
HR-20	Dec. '77	Effects of Hazardous Material Spills on Biological Treatment Processes	EPA - 600/2-77-239 NTIS - PB-276 724/2BE PC A10/MF A01
HR-21	Mar. '78	Development of a Kit for Detecting Hazardous Material Spills in Waterways	EPA - 600/2-78-055 NTIS - PB-281 284/0BE PC A05/MF A01
HR-22	Apr. '78	Hazardous Material Spills: A Documentation and Analysis of Historical Data	EPA - 600/2-78-066 NTIS - PB-281 090/1BE PC A11/MF A01
HR-23	Jul. '78	System for Applying Powdered Gelling Agents to Spilled Hazardous Materials	EPA - 600/2-78-145 NTIS - PB286 308/2 BE PC A03/MF A01
HR-24	Mar. '79	Selected Methods for Detecting and Tracing Hazardous Material Spills	EPA - 600/2-79-064 NTIS - PB-298 054/8BE PC A04/MF A01
HR-25	Jul. '79	Comparison of Three Waste Leaching Tests	EPA - 600/2-79-071 NTIS - PB-299 259/2BE PC A11/MF A01
HR-26	May '79	Background Study on the Development of a Standard Leaching Test	EPA - 600/2-79-109 NTIS - PB-298 280/9BE PC A12/MF A01
HR-27	Chem. Stf. Pub. '79	Publications on the Analysis of Spilled Hazardous and Toxic Chemicals and Petroleum Oils	EPA - OHMSB
HR-28	Aug. '79	Acoustic Monitoring to Determine the Integrity of Hazardous Waste Dams	EPA - 625/2-79-024 NTIS - PB-80-176787
HR-29	Jan. '80	CAM-4, Portable Warning Device for Organophosphate Hazardous Material Spills	EPA - 600/2-80-033 NTIS - PB-80-159494

HR-30	May '80	Environmental Emergency Response Unit Capability	EPA - OIRMBS
HR-31	May '80	Application of Buoyant Mass Transfer to Hazardous Materials Spills	EPA - 600/2-80-078 NTIS - PB-80-198427
HR-32	May '80	Alternate Enzymes for Use in Cholinesterase Antagonist Monitors ("CAM's")	EPA - 600/2-80-083 NTIS - PB-80-209835
HR-33	Jul. '80	Hazardous Material Spills and Responses for Municipalities	EPA - 600/2-80-108 NTIS - PB-80-214141
HR-34	1981	Detection and Mapping of Insoluble Sinking Pollutants	
HR-35	1981	Use of Selected Sorbents and Aqueous Film Forming (AFF) Foams on Floatable Hazardous Material Spills	
HR-36	May '81	Development of a System to Protect Groundwater Threatened by Hazardous Spills on Land	EPA - 600/2-81-085 NTIS - PB-81-209587 PC A07/MF A01
HR-37	1981	Removal of Water-Soluble Hazardous Materials Spills from Waterways by Activated Carbon	
HR-38	1981	Guidelines for the Use of Chemicals in Removing Hazardous Substance Discharge	
HR-39	1981	Restoring Hazardous Spill-Damaged Areas: Identification and Assessment of Techniques	
HR-40	1981	A Mobile Stream Diversion System for Hazardous Materials Spills Isolation	
HR-41	1981	Modifications of Spill Factors Affecting Air Pollution	
HR-42	1981	Removal of Spilled Hazardous Materials from Bottoms of Flowing Watercourses: Phase I	
HR-43	1981	Feasibility of Commercialized Water Treatment Techniques for Concentrated Waste Spills	

NATIONAL CONFERENCE ON CONTROL OF HAZARDOUS MATERIAL SPILLS

<u>OWMSB Code</u>	<u>Title/Date/Place</u>
HP-1	Proceedings of the 1972 National Conference on Control of Hazardous Materials Spills. March 21-23, 1972, Houston, Texas.
HP-2	Proceedings of the 1974 National Conference on Control of Hazardous Material Spills. August 25-28, 1974, San Francisco, California.
HP-3	Proceedings of the 1976 National Conference on Control of Hazardous Material Spills. August 25-28, 1976, New Orleans, Louisiana.
HP-4	Proceedings of the 1978 National Conference on Control of Hazardous Materials Spills. April 11-13, 1978, Miami Beach, Florida.
HP-5	Proceedings of the 1980 National Conference on Control of Hazardous Materials Spills. May 13-15, 1980, Louisville, Kentucky.
HP-6	Proceedings of the 1980 US EPA National Conference on Management of Uncontrolled Hazardous Waste Sites, October 15-17, 1980, Washington, D.C.

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GLOSSARY

The geologic, hydrologic, and chemical terms pertinent to this report are defined as follows:

Aqueous Phase - water in the saturated or unsaturated zone, which may contain hydrocarbon compounds (see Hydrocarbon Fluid Phase; Hydrocarbon Solid Phase).

Aquifer - a formation, group of formations, or part of a formation that contains sufficient saturated permeable material to yield significant quantities of water to wells or springs.

Confined Ground Water - ground water under pressure significantly greater than atmospheric. Its upper limit is the bottom of a bed of distinctly lower vertical hydraulic conductivity than that of the material in which the confined water occurs (see "Confining Bed").

Confining Bed - a body of material with low vertical permeability stratigraphically adjacent to one or more aquifers. Replaces the terms "aquiclude," "aquitard," and "aquifuge."

Desorption - the removal of contaminants from the solid matrix of the porous medium by fluids in the ground water system.

Diffusion - molecular movement of chemical constituents of ground water or hydrocarbon fluids in response to chemical-concentration gradients.

Dispersion, Mechanical - differences in the rate and direction of movement of individual tracer particles owing to variations in path lengths, and pore geometry or size.

Dispersion, Hydrodynamic - the combined effects of "Diffusion" and "Dispersion, mechanical."

Drawdown - the vertical distance between the static (nonpumping) water level and the level caused by pumping.

Ground Water - that part of subsurface water that is in the saturated zone.

Head, Static - the height above a standard datum of the surface of a column of water that can be supported by the static pressure at a given point.

Hydraulic Conductivity - capacity of a rock to transmit water under pressure. It is the rate of flow of water at the prevailing kinematic viscosity passing through a unit section of area, measured at right angles to the direction of flow, under a unit hydraulic gradient (see "Permeability, Intrinsic").

Hydrocarbon Fluid Phase - a liquid mixture of hydrocarbon compounds, immiscible with water, that forms a fluid phase physically distinct from the aqueous phase. It is distinctly denser and more viscous and has a higher surface tension than the aqueous phase. (See Aqueous Phase; Hydrocarbon Solid Phase.)

Hydrocarbon Solid Phase - hydrocarbon compounds sorbed onto the matrix of the porous media. (See Aqueous Phase; Hydrocarbon Fluid Phase; Sorption.)

Isopotential Line - line connecting points of equal static head. (Head is a measure of the potential.)

Multiaquifer Well - any well that hydraulically connects more than one aquifer. The connection may be due to original open-hole construction or to deterioration of casing or grout seal.

Permeability, Intrinsic - a measure of the relative ease with which a porous medium can transmit liquid under a potential gradient. It is a property of the medium alone and is independent of the nature of the liquid and of the force field causing movement. It is a property of the medium that is dependent upon the shape and size of the pores.

Piezometer - a small-diameter pipe placed in the ground in such a way that the water level in the pipe represents the static head at the very point in the flow field where the piezometer terminates.

Porosity - the property of a rock or soil to contain interstices or voids. It may be expressed quantitatively as the ratio of the volume of interstices to total volume of the rock. (See "Porosity, Effective.")

Porosity, Effective - the amount of interconnected pore space available for fluid transmission. It is expressed as a decimal fraction or as a percentage of the total volume occupied by the interconnecting interstices.

Potentiometric Surface - a surface that represents the static head. As related to an aquifer, it is defined by the levels to which water will rise in tightly cased wells. Where the head varies appreciably with depth in the aquifer, a potentiometric surface is meaningful only if it describes the static head along a particular specified surface or stratum in that aquifer. More than one potentiometric surface is then required to describe the distribution of head. The water table is a particular potentiometric surface. Replaces the term "Piezometric Surface."

Saturated Zone - zone in earth's crust in which all voids are ideally filled with water. The water table is the upper limit of this zone. Water in the saturated zone is under pressure equal to or greater than atmospheric.

Sorption - the removal of contaminant from fluids in the ground water system by the solid matrix of the porous medium.

Specific Capacity - the rate of discharge of water from a well divided by the drawdown of water level within the well. It varies slowly with duration of discharge, which should be stated when known. If the specific capacity is constant except for time variation, it is roughly proportional to the transmissivity of the aquifer.

Specific Yield - the ratio of the volume of water that a saturated rock or soil will yield by gravity to its own volume.

Storage Coefficient - the volume of water an aquifer releases from or takes into storage per unit surface area of the aquifer per unit change in head. In an unconfined aquifer, it is virtually equal to the specific yield.

Transmissivity - the rate at which water of the prevailing kinematic viscosity is transmitted through a unit width of an aquifer under a unit hydraulic gradient.

Unconfined Ground Water - water in an aquifer that has a water table.

Valley Fill - drift or alluvial sediments deposited in an erosional depression in the bedrock surface.

Water Table - that surface in an unconfined water body at which the pressure is atmospheric. It is defined by the levels at which water stands in wells that penetrate the water body just far enough to hold standing water. In wells that penetrate to greater depths, the water level will stand above or below the water table if an upward or downward component of ground water flow exists.

Well Field - as used in this report, any combination of wells withdrawing water from the same area and close enough to cause mutual drawdown effects.

Zone, Saturated - that part of the water-bearing material in which all voids, large and small, are ideally filled with water under pressure greater than atmospheric. The saturated zone may depart from the ideal in some respects. A rising water table may cause entrapment of air in the upper part of the zone of saturation, and some parts may include accumulations of other fluids.

Zone, Unsaturated - the zone between the land surface and the water table. It includes the capillary fringe. Characteristically, this zone contains liquid water under less than atmospheric pressure and water vapor and air or other gases generally at atmospheric pressure. In parts of the zone, interstices, particularly the small ones, may be temporarily or permanently filled with water. Perched water bodies may exist within the unsaturated zone and some parts may include accumulations of other fluids. Replaces the terms "zone of aeration" and "vadose zone."

APPENDIX A

COSTS ASSOCIATED WITH WASTE DISPOSAL SITE CLEANUP

COSTS ASSOCIATED WITH WASTE DISPOSAL SITE CLEANUP

The enclosed cost information describes the costs of various aspects of the contamination assessment and remedial action programs as well as some examples of costs associated with actual instances of groundwater contamination. Many of the costs are representative of rates prevailing in the northeastern United States in the mid 1970s to early 1980s and actual costs may be higher or lower depending on local conditions. The purpose of the cost information is to indicate the potential magnitude of the expense associated with site cleanup as well as the relative cost of the various phases.

TABLE A-1. COST ESTIMATES FOR VARIOUS MONITORING TECHNIQUES AND CONSTRUCTION METHODS IN THE ZONE OF SATURATION (FROM U.S. EPA, 1980)

Monitoring Technique & Construction Method	Price Per Installation Well Diameter		
	51mm (2-inch)	102mm (4-inch)	152mm (6-inch)
Screened over a single interval (plastic screen and casing)			
1. Entire aquifer	\$1,600-\$3,700	\$2,300-\$4,500	\$6,400-\$7,500
2. Top 3 meters (10 feet) of aquifer	600- 1,050	700- 1,150	-
3. Top 1.5 meters (5 feet) of aquifer with drive point	100- 200	-	-
Piezometers (plastic Screen & casing)			
1. Entire aquifer screened			
a. Cement grout	2,100- 4,700	2,800- 5,500	6,900- 8,500
b. Bentonite seal	1,850- 4,150	2,350- 4,950	6,650- 7,950
2. Top 3 meters (10 feet) of aquifer screened			
a. Cement grout	1,150- 2,050	1,200- 2,150	-
b. Bentonite seal	900- 1,500	950- 1,600	-
Well clusters			
1. Jet-percussion			
a. Five-wall cluster, each wall with a 6-meters (20-foot) long plastic screen	2,300- 3,800	-	-
b. Five-wall cluster, each wall with only a 1.5-meters (5-foot) long plastic screen	1,700- 2,300	-	-
2. Augers			
a. Five-wall cluster, each wall with a 6-meters (20-foot) long stainless steel wire-wrapped screen	4,600- 5,300	-	-
b. Five-wall cluster, each wall with only a 1.5-meters (5-foot) long gauge-wrapped drive points	1,600- 2,600	-	-
3. Cable tool			
a. Five-wall cluster, each wall with a 6-meters (20-foot) long stainless steel, wire-wrapped screen	-	-	9,850-14,150
4. Hydraulic rotary			
a. Five-wall cluster, each wall with a 6-meters (20-foot) long plastic screen, casing grouted in place	-	9,050-14,900	13,800-19,400
b. Five-wall cluster, completed in a single large-diameter borehole 4.5 meters (15-foot) long plastic screens, 1.5-meters (5-foot) seal between screens	4,240- 5,880	8,250-11,000	-
5. Single wall/multiple sampling point			
a. 13.5 meters (110-foot) deep wall with 1-foot long screens separated by 1.2 meters (4 feet) of casing starting at 3 meters (10 feet) below ground surface	-	-	1,000- 4,700
Sampling during drilling	-	3,300- 4,700	3,300- 5,200

Cost estimates are for an aquifer composed of unconsolidated sand with a depth to water of 3 meters (10 feet) and a total saturated thickness of 30 meters (100 feet). Cost estimates are based on rates prevailing in the Northeast in Autumn, 1975. Actual costs will be lower and higher depending upon conditions in other areas. Therefore, while the costs presented will become outdated with time, the relative cost relationships among the monitoring techniques should remain fairly constant.

EXAMPLES OF UNIT COSTS FOR SITE CLEAN-UP

VEHICLES

- Front Loader: \$300/day
- Backhoe: \$225/day
- Small Bulldozer: \$225/day
- Vacuum Trucks: \$50/hr
- Light Trucks: \$30/day
- Heavy Trucks: \$100-200/day

SAMPLE COLLECTION FROM WELLS, SOILS, STREAMS

- 1-2 hrs/well
- 2-3 person crew
- Truck, pumps, containers
- \$50-200/sample

SAMPLE ANALYSIS

- \$30-60/sample/parameter for conventional pollutants
- GC/MS priority pollutants: \$900-2000/sample
- GC/ECD pesticides: \$100-350/sample
- ICAF metals: \$100-350/sample

CLEAN-UP CREW (8-10)

- Supervisor (1), Chemist (1), Technician (1), Equipment Operators (2-3), Laborers (3-4)
- ~ \$250-300/hr (\$2000 - 2400/day)

BARRELS

- Disposal: \$75-300 each
- Repackaging: \$100 each

DAILY COSTS FOR SITE CLEAN-UP (EXAMPLE)

- | | |
|---------------------|---------------|
| - Crew | \$2000 |
| - Equipment | \$1000 |
| - Sampling/Analysis | \$1000 |
| - Barrel Costs | <u>\$1000</u> |
| | \$5000 |

YEARLY COST AT ABOVE RATE (EXAMPLE): \$1,200,000 (2400)

SPECIAL EXPENSES

- Site Access/Preparation
- Utilities
- Fences, Security
- Administration
- Insurance
- Inspection

YEARLY COST + SPECIAL COSTS: \$1,500,000 + (?)

TYPICAL REMEDIAL ACTION COSTS*

		COST (MID 1980 \$)		UNITS
ACTION		MED. SIZE LANDFILL	MED. SIZE IMPOUNDMENT	
1A.	Contour grading and surface water diversion	8,000	-	/AC
1B.	Pond closure and contour grading	-	20,000	/AC
2.	Surface sealing	34,000	25,000	/AC
3.	Revegetation	7,000	2,000	/AC
4.	Bentonite slurry-trench cutoff wall	9	9	/FT ²
5.	Grout curtain	150	57	/FT ²
6.	Sheet piling	9	11	/FT ²
7.	Bottom sealing	3,600,000	640,000	/AC
8.	Drains	120	560	/FT
9.	Well point system [†]	13	33	/FT ²
10.	Deep well system [†]	3.2	13	/FT ²
11.	Injection [†]	166	12	/FT ²
12.	Leachate handling by sub-grade irrigation	9,100	-	/AC
13.	Chemical fixation	52,000	-	/AC
14.	Chemical injection	0.1	-	/FT ³
15.	Excavation and disposal at secure landfill	3.5/FT ³	1.5/GAL	
16.	Ponding	370	-	/AC
17.	Trench construction	6	-	/FT
18.	Perimeter gravel trench	40	-	/FT
19.	Treatment of contaminated groundwater	15	27	/GAL
20.	Gas migration control ^{††}			
	Passive	300	-	/FT
	Active	70	-	/FT
21.	Berm construction	-	4	/YD ³

[†]Units: \$ per intercept face area

^{††}Units: \$/Length (ft) of site perimeter

*Source: U.S. EPA, Cost of Remedial Response Actions at Uncontrolled Hazardous Waste Sites. Report to MERL, Cincinnati, Ohio.

EXAMPLES OF CLEAN-UP COSTS AT ACTUAL SITES
(not all costs are final)

- OLIN CORP/REDSTONE ARSENAL MILITARY RESERVATION (AL)
 - Dichlorodiphenyltrichloroethane (DDT) contamination of surface waters used for water supply. Produced from 1947-1970. Sued in 1970.
 - Wastewater discharge was permitted.
 - High levels of DDT found in soil, water, fish, near site.
 - U.S. Army Corps of Engineers commissioned a \$1.3 million study of problem and possible corrective action (1979).
 - Estimated 837 tons of DDT in sediments of stream.
 - Suggested rerouting stream; estimated cost: \$88.9 million.
 - TVA was authorized to spend \$1.5 million on special studies/local aid in 1981.
- CHEM-DYNE HAZARDOUS WASTE DUMP (OH)
 - Approximately 20,000 drums of chemicals at site.
 - Pollution of surface and groundwater, soil, air; fires.
 - EPA negotiated agreement with 109 companies for partial clean-up. Other generators identified.
 - Cost: \$2.4 million (\$250,000 by Velsicol).
 - Justice Department suing mine owner/operators plus 16 waste contributors.
- LOVE CANAL (NY)/HOOKER CHEMICAL CORPORATION
 - Abandoned canal used for disposal of chemicals (1942-1953) (21,000 tons)
 - Sold land to Niagara Falls Board of Education in 1953 for \$1.00.
 - Problem identified in 1978 (surface breakthrough).
 - Settlement agreement for clean-up negotiated cleaned-up cost: \$62 million.
 - Suits asking for compensatory and punitive payments total several billion dollars.

- W. R. GRACE & COMPANY, ACTON, MASS.
 - Organic chemicals contaminated Acton town wells.
 - Wells 1500 ft. from waste lagoons.
 - Initial hydrogeological study: \$90,000 - \$140,000.
 - Findings criticized by Grace; second hydrogeological study paid for by company (\$?).
 - Consent decree signed with state in October 1980 for 20-30 year clean-up of aquifer.
 - Company being sued for \$22M by Acton Water Board.

- SUPERFUND ALLOCATIONS
 - Picillo Farm (RI): \$4.9M
 - Kim-Buc Landfill (NJ): \$2.44M (Removal)
 - Love Canal (NY): \$5.3M
 - Commencement Bay (WA): \$0.718M (Site investigations)